Spiraling in Fluorescent Lamps[1]

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ABSTRACT

Factors which produce or affect spiraling in low pressure discharges are discussed and studied in tubes of normal fluorescent lamps and of special design. The order of magnitude of the forces in a discharge is calculated from magnetic deflection measurements. Tension forces in one constricted but not spiraling type of discharge were found to be about 10 to 30 dynes. Spectroscopic study of the constricted and magnetically distorted plasma revealed the presence of barium, strontium, and probably calcium. Langmuir, *et al.'s* theory of the constricting sheath has been applied with the modification that in fluorescent lamps the sheath is believed to be caused by sputtered alkaline earth vapors or aggregates instead of tungsten vapors or aggregates, while the role of carbon aggregates is still uncertain.

Introduction

When a fluorescent lamp burns normally, the flow of electrons through the plasma proceeds quite regularly and extends to the walls of the tube. The arc voltage remains constant.

Sputtering of the electrodes produces a constriction in the discharge. With half-coated lamps one can observe a decrease of the plasma's diameter while the arc voltage increases. However, there is a limit in this constriction beyond which the discharge ceases to be rectilinear. Waves appear in the arc and finally the thin discharge stream begins a spiraling or swirling movement which may continue for hours. While the arc swirls, its voltage fluctuates by more than 30 per cent. With coated tubes a photocell shows periodic variations in light intensity of 100 per cent or more.

Kenty and Cooper (1) found that the introduction of ethylene into a lamp caused much spiraling which was attributed to carbon resulting from the decomposition of ethylene. Earlier, Langmuir, Found, and Dittmer (2) had described a "streamer discharge" which shows many analogies with the spiraling discharge, although the latter phenomenon was not mentioned. The argon pressure in these authors' device was 2 to 4 mm Hg. Free mercury was not deliberately introduced, and the electrodes were not of the activated type. The tungsten electrode filament was heated to 2500°K and an arc of 1 amp was passed through the tube, filling it with a uniform reddish glow. By opening the cathode heating circuit for one-half second, the cathode temperature was lowered, the cathode drop increased, and tungsten was sputtered into the arc. "The small dose of tungsten vapor has a profound effect on the arc. The arc begins to detach itself from the walls." Its diameter diminishes gradually. The constricted arc is very sensitive to magnetic fields and can be easily deflected by a weak magnet. The formation of small, golden yellow droplets is described. The blue tungsten spectrum was observed during the first 30 seconds after the vaporization of the cathode. By sputtering molybdenum, tantalum, or carbon into the arc, similar phenomena can be obtained, "but they seem to be more striking and more persistent with tungsten."

Streamer Discharge and Spiraling

In fluorescent lamps it is not necessary to heat the electrode filaments as high as 2500°K because they are activated by alkaline earth oxides. An arc strikes at filament temperatures of 1100°K or even lower. Frequently spiraling appears simultaneously with starting. This effect may continue for hours or days, and restarting is not necessary to produce it. Although the activation of the electrodes was done quite carefully in our experiments, free carbon did remain in the activated cathodes under certain conditions.

Assuming that a streamer discharge may be considered as a first step toward spiraling, how can one explain the occurrence of such striking and persistent spiraling even in the absence of tungsten vapor? From the work reported below it does not seem likely that the spiraling is caused by traces of carbon on the electrodes which were not completely eliminated during the heat treatment in vacuo. However, even assuming that these traces of carbon are sufficient to produce the effect, how could the latter be so persistent in view of the finding of Langmuir, *et al.*, that

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the constriction phenomena are less persistent with carbon?

Tube Diameter and Walls

In tubes coated with silicate phosphors spiraling was found to be less persistent than in uncoated tubes. In order to stop spiraling altogether, the best method is to stop the arc current for a while and then to restart the arc. We found that the time of interruption necessary to eliminate spiraling is much longer with uncoated tubes than with silicate coated tubes. With uncoated tubes of 40 mm diameter spiraling was observed to go on for days, while it diminished gradually and sometimes disappeared after one hour or less in coated tubes. Likewise, the length of current interruption required to stop spiraling was of the order of a minute or less for silicate coated tubes, but much longer with uncoated tubes.

Finely divided silicates have a well-known adsorbing power. Thus the elimination of sputtered matter from the gas phase may be more rapid and more efficient than with a glass surface. While the lamp burns the silicates gradually adsorb the impurities and so stop spiraling with their complete elimination from the gas phase. This surface adsorption thus works against the electrical forces which tend to hold sputtered matter in the gas phase. When the lamp is turned off, electrical forces are no longer present and sputtered matter can diffuse toward the walls, and be adsorbed there. Clean glass surfaces have a lower adsorbing power and can not overcome the electrical forces. When a clear lamp is turned off, sputtered matter will not condense quite as efficiently. Therefore, spiraling is not as effectively stopped in clear tubes.

Before these experiments were run, however, it had to be established whether the nature of the walls as such had some specific influence upon spiraling. For this purpose a sheet of copper foil 0.3 mm thick and 100 mm long was laid against the inner wall of a glass tube of 40 mm diameter and 100 cm length. Ordinary activated electrodes were sealed at the two ends and the tube baked and exhausted as usual. The bright metal foil was found to have no effect on the spiraling discharge. The blue luminous ribbon which was swirling along the tube was not disturbed by the presence of the copper.

The diameter of the glass tube, however, does have some effect. In narrow tubes spiraling is more easily produced and with smaller amounts of sputtered matter. With increasing tube diameter higher pressures of argon are necessary to produce swirling. In nearly all cases spiraling started right at the electrodes presumably as a result of the sputtering from the electrodes.

The above observations and theories were arrived at during other studies on fluorescent lamps and have not been the subject of systematic statistical research. They are pointed out here merely because they led to experiments, described later, and directed toward the principal aims of this investigation, namely, to find out what the nature of the impurities is, where the sputtered matter is located during spiraling, why it cannot be observed on ordinary spectrograms, and, finally, what the relationship is between contriction of the plasma and spiraling.

Forces in the Constricted Plasma

Considering the plasma itself, the following three types of discharge may be distinguished:

(1) No sputtering occurs at the electrode. The plasma is very large and extends toward the walls of the tube even with diameters as large as 100 mm (Fig. 1*a*).

(2) Some sputtering occurs when the arc is started. The diameter of the plasma decreases and it becomes sensitive to a magnet (Fig. 1*b*). With a tube diameter of 40 mm the arc remains linear. With larger tube diameters, such as 100 mm, the arc bends upward owing to convection forces in the argon.

(3) Continued sputtering brings about further constriction and increases the sensitivity to a magnet. Beyond a certain limit in this constriction the discharge loses its stability even in the absence of a magnet. In narrow tubes it begins to wave and spiral; in wide tubes it first bends up until it touches the upper wall and then also begins to swirl (Fig. 1*c*).

During the spiraling, the arc voltage increases. For example, a tube of 38 mm diameter and 120 cm length, filled with argon at 3.75 mm Hg, showed an arc voltage of 112 volts between the electrodes during a normal run without spiraling (first type of discharge). When spiraling occurred, the arc voltage increased to 120 or 130 volts or even higher (third type of discharge). With small constrictions (second type) an increase of a few volts was observed. This increase measures what we shall call a "tendency to spiraling."

A useful analogy may be a comparison of the discharge with a rubber cylinder stretched between the two electrodes, in which four different forces shall be distinguished:

A. The "pinch effect."—Assuming that the conducting column of the arc consists of concentric shells or, better yet, of conducting filaments, all these shells or filaments except the one coinciding with the axis will experience a force which, if free to act, will direct them toward the axis of the plasma. This is the so-called "pinch effect."

If the electrodes were mobile, the plasma would contract so as to diminish in cross section and, consequently, increase in length. If the electrodes are not

mobile as in the present case, a certain pressure will be exerted upon them which tends to increase the length of the plasma.

Let R be the radius of the plasma considered to be cylindrical, and r the radius of any imaginary internal cylinder. Then the inward radial pressure f_i

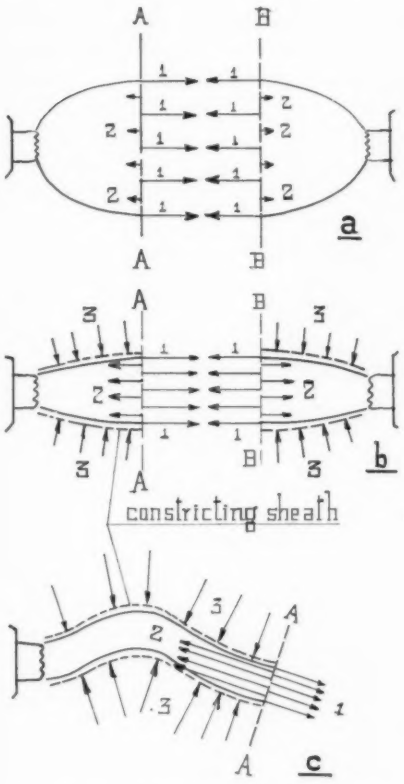

FIG. 1. *a:* Nonconstricted plasma. Forces "1" represent tension forces, "2" repulsion forces. AA and BB are imaginary sections in the plasma. *b:* Constricted plasma. Forces "2" are smaller than forces "1." The increase in electron density is not sufficient to produce spiraling. Forces "3" are the constricting forces. *c:* Constriction beyond the limit starts spiraling. Forces "2" are greater than forces "1."

per unit area, at any distance r from the axis of the column, is given by the expression (3):

$$f_i = \frac{I^2}{R^4}(R^2 - r^2)$$

where I is the current per unit cross section which is assumed to be constant over the section. Assuming that the radial pressure is transmitted along the axis without change, the total hydrostatic force F on the electrodes can be found easily. Integrating for all values of r from 0 to R gives:

$$F = \int_0^R \frac{I^2}{\pi R^4}(R^2 - r^2)2\pi r\, dr = \frac{I^2}{2}$$

In fluorescent lamps where the current is less than 0.5 amp this force F will not exceed 0.005 dynes. Compared with the forces studied later, the "pinch effect" may be neglected.

B. Reaction forces on the electrode.—These were studied by Mason (4), Kobel (5), Myer (6), and others. A molecule of mass m, leaving the electrode with component velocity u_x in the direction normal to the electrode, has a momentum mu_x which exerts a reaction force f_r on the electrode. The total reaction on the electrode shall be proportional to the rate of loss of cathode matter. With copper electrodes values of 189 to 435 dynes were found for currents of 11 to 32 amp.

It can be seen that these forces decrease rapidly with current. In fluorescent lamps with activated cathodes the loss of matter is negligible. Since the currents remain below 1 amp, the reaction forces may be neglected here also.

C. Convection forces.—These bend the column upward at times, while the discharge remains a steady arc. As these forces are difficult to calculate at different pressures and temperatures, we have measured them indirectly as will be discussed below.

D. Constriction forces.—None of the above forces can explain the constriction observed in fluorescent tubes. Langmuir, *et al.*, state that negatively charged, sputtered tungsten particles and atoms can not deposit on the walls. They remain between the arc and walls. "Near the boundary of the arc there must be an electric double layer consisting of an inner sheath having positive space charge and an outer sheath with a negative charge." The tube containing a streamer discharge forms a sort of skin which scatters light. The latter appears to be completely polarized when observed at right angles to incident light. "No scattered light is detected in the interior of the arc; there is some light scattered from the whole of the nonluminous gas outside the arc, but the intensity increases rapidly as the skin is approached."

In fluorescent lamps, spectroscopic study (see below) showed that this sheath is formed by alkaline earth vapors and perhaps by carbon.

The following facts should now be considered jointly: (*a*) At constant current the arc cross section decreases with increasing amounts of sputtered matter; (*b*) Interruption of the current flow allows vapors to condense with a resulting increase of the arc cross section after the arc has been restarted, this elimination of sputtered matter being more effective in silicate coated tubes; (*c*) In small diameter tubes constriction of the arc and spiraling are easier to obtain than in wide tubes; walls repulse the sheath which is in equilibrium between them and the plasma.

From these observations it must be concluded that

the decrease of the plasma cross section is the result of constricting radial forces which are exerted by the vapor sheath surrounding the discharge column, the sheath itself being repulsed by the walls. The constriction is followed by an increase in electron density which is accompanied by axial forces, i.e., repulsions toward the electrodes. These repulsions tend to increase the length of the column in like manner as the "pinch effect."

Within certain limits of constriction the effect of the repulsive forces will be to compensate partially for the attractive forces due to the electrical potential gradient, thus stretching the arc and reducing its tension (Fig. 1*b*). When this compensation is only partial, the arc remains rectilinear but is more sensitive to magnetic deflection. If the constriction is sufficient to compensate completely for the attractive tension, then the arc becomes unstable.

Beyond this limit, a further constriction through additional sputtering will cause a stronger decrease in cross section of the plasma. The repulsive forces become now greater than the attractive tensions (Fig. 1*c*) and the discharge column will tend to increase its length by a waving movement which rapidly changes into swirling. With the aid of a concentrically placed magnetic coil around the tube, the direction of rotation of the discharge around the magnetic field of the coil may be determined, the latter following Ampere's rule. If the current in the coil is reversed, the rotation of the discharge (the blue ribbon) is also reversed. This experiment requires direct current in the tube and a few gauss are sufficient for it.

Experimental Data

In order to determine the order of magnitude of the forces discussed above, we measured electromagnetic deflections of constricted arcs with our simple device equipped with fixed electrodes as shown in Fig. 2*a*. Two activated tungsten filaments such as those used in fluorescent lamps were mounted at the ends of a glass tube of 100 mm diameter. The distance between the electrodes was 130 mm. The tube was well baked and exhausted.

Pure argon was introduced and the experiments were then carried out both in the presence and in the absence of mercury. The presence of mercury has no effect upon constriction. The arc voltage measured about 50 volts. The diameter of the plasma was not sharply defined and was measured only approximately. Identical coils were then placed at each side of the tube so that their magnetic field was normal to the axis of the tube. Three different experiments were then carried out.

(1) The cathode filament was heated to some 1000°K and 220 volts tension was applied. If the electrode activation was good and the purity of the argon adequate, the arc started without sputtering. The plasma spread out to the walls of the tube. A magnetic field of 150 gauss caused only a negligible deflection which was not measurable.

(2) Heating of the filament was interrupted for a fraction of a second. Sputtering commenced and the diameter of the cross section fell to 20 mm or even as low as 8 mm. The arc appeared as a blue ribbon and was bent upward. It remained fixed at the two electrodes and presented what shall be called a "convection deflection" of 12 mm. When current was passed through the coils so as to direct the electromagnetic force upward, the deflection increased to 20, 30, or 40 mm. A run of measurements was taken for different magnetic fields. To each field corresponded a deflection and an increase in arc length. Here distinction shall be made between the initial lengthening due to convection, and the lengthening corresponding to the supplementary electromagnetic bending.

TABLE I (Curve I*a*)

Field H in gauss	Deflection d in mm	Lengthening L in mm	Electromagnetic force F in dynes	Total force ΔF in dynes
0	12	2.9	0	22.8
30	0	0	22.8	0
30	20	8	22.8	45.6
37.4	23	10.5	28.5	51.3
42.8	25	12.4	32.5	55.3
55	30	17.9	41.8	64.6
67.5	32	20.5	51.2	74.0
85	33	21.5	64.5	87.3
92.5	37	26.5	70.2	93
125.5	42	32	95	117.8

TABLE II (Curve I*b*)

30	0	0	22.8	0
40	5	0.50	30	7.2
42.5	11	2.48	32	9.2
49	14	3.9	37.2	14.4
55	17	5.6	41.7	16.7
65	21	8.9	49.4	26.6
110	25	12.4	82.5	54.5

For a given cross section, arc current, and argon pressure, there is a definite value of the magnetic field strength which straightens the arc to a linear column. This downward electromagnetic force is approximately equal to the convection current bending force. Table I gives the data of these measurements, and Table II gives the data for measurements with electromagnetic forces directed downward.

In the first column of the tables the magnetic field is calculated in gauss. As an approximation the field is assumed to be uniform. In the second column, d

represents the arc deflection measured at the middle of the arc. L in the third column represents the lengthening of the arc assuming that the arc curve is circular. Since the distance between electrodes remained constant in our experiments, a different radius had to be ascribed to each deflection. In the fourth column, F is the electromagnetic force resulting from the interaction between magnetic field and arc current.

In Table I the fifth column gives the sums ΔF of the electromagnetic forces and the upward convection forces. For example, for $H = 0$ and $F = 0$ the deflection is 12 mm. For $H = 30$ gauss the electromagnetic force F is 22.8 dynes directed downward to neutralize the convection deflection, $L = 0$, and $\Delta F = 0$ referring to the difference between the two opposing forces. In the third and following lines the electromagnetic force F must be added to the convection force of 22.8 dynes. In Table II these 22.8 dynes are subtracted from the electromagnetic force F because the latter is directed downward.

Fig. 2 shows the curves obtained when the increase in arc length is plotted against the total vertical deflecting forces. Upward deflections are plotted as positive ordinates, downward deflections as negative ordinates.

The curves I were taken for arc currents of 750 ma at an argon pressure of 23 mm. The cross section had decreased from 100 to 10 mm. The values for the abscissa for curve Ib were taken from the fifth column of Table II. The convection forces were subtracted for Ib. Since these convection forces seem to be less effective when the arc is bent downward, curve Ic was also drawn in the figure, for which the convection forces have not been subtracted. Ia and Ic intercept the abscissa at a point corresponding to 30 dynes where no deflection occurs.

The bent plasma is in equilibrium between the vertical force ΔF and the tension T which fixes the arc to the electrodes. If the plasma may be considered to behave like an elastic steel ribbon, Fig. 3a shows the graphical method adopted to calculate approximately the tension on the electrodes which would balance the vertical forces. The values found are plotted in Fig. 3b against the vertical forces ΔF;

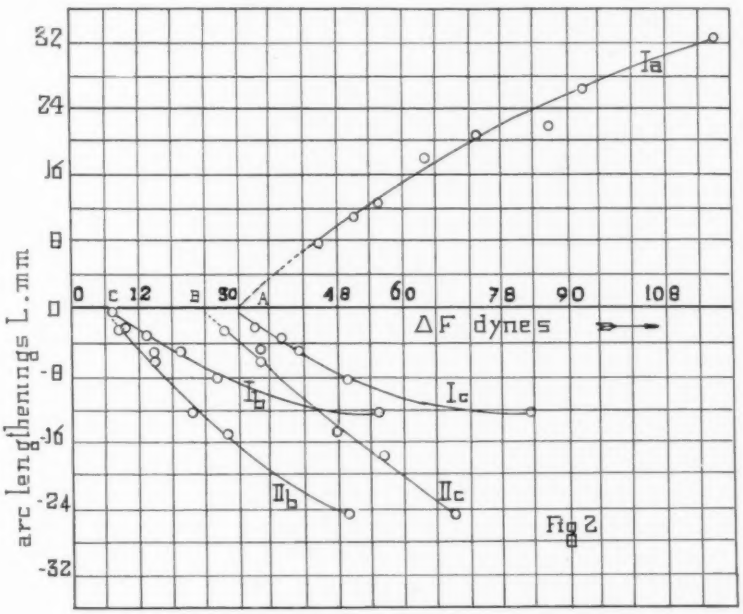

FIG. 2. Increase in arc length as a function of total force ΔF

22.8 dynes which produce a deflection of 12 mm are balanced by 62 dynes tension at one electrode; 55.3 dynes total vertical force corresponding to a deflection of 25 mm are balanced by 74.8 dynes at each electrode. The curve intersects the ordinate at the point 50 dynes which is the value of the tension at each electrode when the plasma is not deflected. The curve is lowered by a new constriction of the plasma, and the limit at which spiraling begins is reached when the curve intersects the ordinate at zero.

The curves II of Fig. 2 refer to an arc of 0.55 amp and an argon pressure of 23 mm. The diameter of the cross section is 8 mm, the arc is more constricted, and points B and C are to the left of A. The repulsive forces compensate the attractive forces more effectively.

Fig. 3 represents the extreme development of the

elastic steel ribbon picture. However, this may carry the analogy too far and the elastic rubber ribbon picture may be nearer to reality. Even this rubber ribbon analogy can not be applied at a distance of 1 cm from the electrodes where the processes are more complex. In considering the total direct forces on the electrodes one would have to distinguish between forces on the cathode and those on the anode.

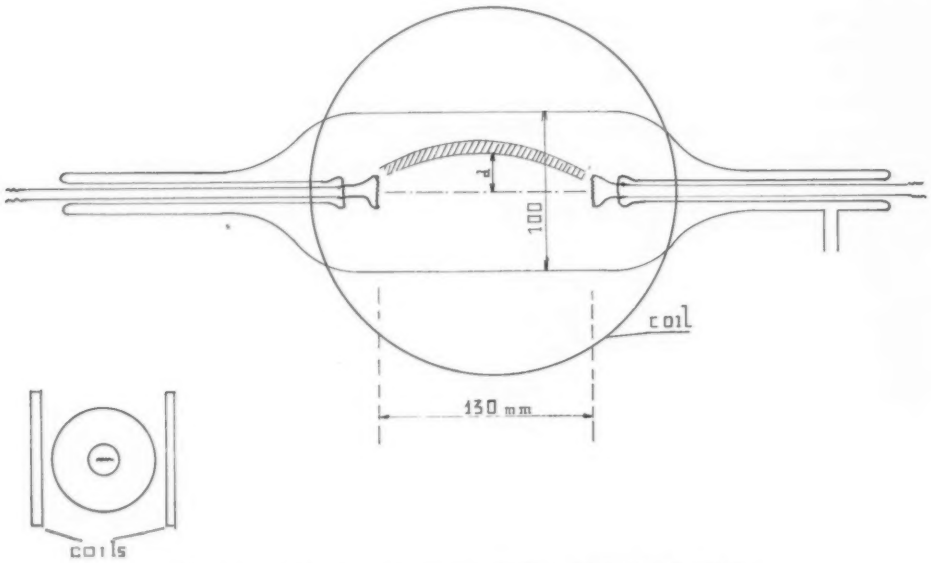

FIG. 2*a*. Device used for measurements of magnetic deflections

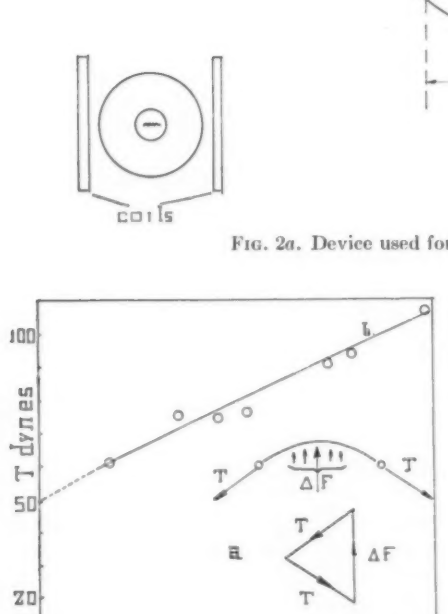

FIG. 3. Tension as a function of total force ΔF

Bombardment by positive ions, the starting period, and the normal discharge would also have to be considered.

It should be pointed out that certain precautions are necessary in order to obtain good curves. During any one run no supplementary sputtering must occur. When a certain constriction is produced, several deflections must be tried till the cross section remains constant. Measurements may begin only after good reproducibility of deflections at zero field is established. Finally, the arc must not be extinguished during the determination of points on any one curve.

Nature of the Constricting Sheath

Kenty and Cooper (1) found that the introduction of ethylene into a fluorescent lamp caused much spiraling. These authors "account for the spiraling as being due to the constrictive effect on the discharge of negatively charged carbon molecules or aggregates of molecules." These authors used also CO and CO_2 in their experiments but no mention of spiraling was made although "a sort of neutral darkening believed to be due to carbon plus HgO" was observed.

We repeated these experiments with carbon dioxide, oxygen, and nitrogen. With CO_2 spiraling was often observed but not always. Mercury oxides were observed as well as velvety black deposits, near the electrodes, which were identified as carbon. A special microanalytical apparatus was constructed in which carbon was oxidized by a chromic-sulfuric acid mixture and the resulting CO_2 identified with barium hydroxide. Oxygen and nitrogen produced no spiraling.

Spectroscopic examination often showed very intense carbon Swan bands although spiraling was not observed at that time and the constriction of the arc was not prominent. In other cases where the Swan bands appeared very faintly spiraling was strong. We believe that the assumption of carbon vapor as being responsible for constriction is only partly tenable. This is confirmed by the following experiment.

A third electrode of tungsten wire covered with a thick coating of alkaline earth carbonates was sealed in the middle of an ordinary fluorescent lamp. After

the lamp had run normally for some time, this auxiliary electrode was heated by a separate heating current. Spiraling appeared, but no deposit of carbon was observable. The usual precautions were taken in preparing the tube, but it is not certain that the carbonates of the auxiliary electrode had been decomposed completely. It seems that the simultaneous presence of carbon and of alkaline earths is a more reliable condition for the appearance of a constricting sheath.

Spectroscopic Investigation

The preceding experiments suggested that alkaline earth vapors sputtered from the electrodes should be very effective in producing spiraling. In the absence of direct evidence for this assumption, a spectroscopic investigation was carried out with the thought to find a difference between the normal and the constricted plasma. Many spectra were taken, both at very close range and at a greater distance from the electrodes. Spectra were taken in the visible, and in the infrared and ultraviolet regions. For the latter purpose discharge tubes of fused silica were used, and photographic plates were chosen which were sensitive to the particular range of wavelengths under investigation. In each case direct comparison was made between the normal and the constricted plasma.

The only method found to make new lines appear in the spectra of constricted or spiraling plasmas consisted in deflecting the discharge column by means of a magnet, and in photographing the spectrum right at the deflected region. The following barium lines were found: 6142, 5853, 5535, 4934 II, 4554 II, and 4130. For strontium: 4607, 4215 II, and 4077 II. A line at 4226 was attributed to calcium.

For some particular positions of the magnet one can observe a yellow light emitted from the plasma's boundary. This light has a continuous spectrum. The skin of the plasma appears to be torn into luminescent yellow aigrettes.

From these experiments it appears that the alkaline earth vapors or aggregates sputtered from the electrodes constitute the principal cause of the constricting sheath. Langmuir *et al.*'s theory of the streamer discharge can be applied here. The aggregates are not visible and do not normally give lines on a spectrogram because they are negatively charged and thus are repulsed from the plasma and from the walls, forming a skin at the boundary of the arc. Magnetic distortion produces local convection currents which project portions of this skin into the discharge column. The vapors or aggregates become excited in the arc and emit their characteristic spectra. The continuous yellow spectrum, mentioned above, is presumably excited by thermal energy furnished by the recombination of ions.

The constriction increases the electronic density in the discharge column, thus creating new internal repulsion forces. There is a limit in constriction for which these repulsion forces neutralize the internal tensions in the arc. Beyond this limit, the repulsive forces exceed the tension forces, the arc tends to increase in length, and spiraling begins.

Conclusion

The spectroscopic study of spiraling in fluorescent lamps has shown that normally there is no difference in the spectra of an ordinary and a constricted or spiraling discharge, the carbon Swan bands appearing in both types. Magnetic distortion of the discharge, however, makes lines of barium, strontium, and calcium appear at positions a certain distance away from the electrodes.

Langmuir *et al.*'s theory of the constricting sheath may be applied but modified to the extent that in fluorescent lamps the sheath is caused by alkaline earth vapors or aggregates instead of tungsten, sputtered from the electrodes. Carbon is also believed to exert a certain yet undetermined influence.

These vapors or aggregates are very effective in constricting the plasma. The constricting power increases with the amount of sputtered matter. In an ordinary 40-watt fluorescent lamp spiraling begins when the constriction reduces the plasma's cross section from 40 to 8 mm. When spiraling occurs, the internal elastic tensions, likened to an elastic rubber ribbon, are neutralized by repulsions due to a 25-fold increase in electron density. Consequently, there is a limit in constriction beyond which the repulsion forces on the electrodes exceed the tension forces. This limit corresponds to the beginning of the spiraling phenomenon. It was not reached in Langmuir *et al.*'s experiments. A study of the relationship between the constriction of the plasma and its deviation by a variable magnetic field showed that in one case where constriction was insufficient to produce spiraling, the tension force was about 10 to 30 dynes.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1950 issue of the Journal.

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Application of the Dropping Mercury Electrode to Diazo Chemistry[1]

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ABSTRACT

The reduction of diazotized aromatic amines has been observed to occur at the dropping mercury electrode. The reduction is irreversible and the polarographic waves are too complex to treat with electrochemical equations. Nevertheless distinct waves whose heights vary directly with concentration are obtained. One wave of the reduction occurs at a potential well below that of the azo or nitro groups or nitrite ion. Therefore, it is possible to use the dropping mercury electrode with an applied potential of 0.3 volt vs. the saturated calomel electrode as an indicator for the measurement of the concentration of diazotized amines. In this manner, amperometric coupling titrations, diazotization rates, coupling rates, etc., may be studied. The new technique is more generally applicable than either the gasometric or colorimetric methods of measuring the concentration of diazotized amines. In certain cases, such as measuring the rapid formation of an insoluble azo compound, the polarographic technique is the only practical method available.

Part I. The Polarography of Diazotized Aromatic Amines

A recent paper (1) described the use of the dropping mercury electrode as an indicator electrode for the amperometric titration of naphthols and related compounds with diazotized aromatic amines. This paper will present further results of the polarographic investigation of diazonium salts in this laboratory. The polarographic reduction of diazotized aromatic amines is far from being simple and cannot be interpreted satisfactorily because the reactions are highly irreversible. Nevertheless, diazotized aromatic amines yield well-defined polarograms whose wave heights are directly proportional to the concentration. The polarograms show that reduction takes place in two main steps, the first at a potential of less than −0.3 volt vs. S.C.E., and the second, usually a much larger wave, at considerably higher voltages. The estimation of diazonium salts is best made by studying the lower wave, which occurs before the nitrite, azo, and nitro group waves. Therefore, it is possible to utilize this wave for following diazotizations, diazo decompositions, couplings, and other reactions involving diazotized aromatic amines in aqueous solutions. The actual determination of the strength of a solution of diazonium salt can be done more accurately by an amperometric titration with a coupler than by direct polarographic measurement. Similarly, the other reactions mentioned above are best followed by applying a constant potential of about −0.3 volt vs. S.C.E. across the electrolysis cell. Thus a continuous record of the concentration of diazonium salt can be obtained. Therefore, it is now possible to measure the concentration of diazonium salts directly without resorting to coupling or decomposition reactions. Examples of the general techniques evolved are presented in subsequent sections.

Experimental

The polarograph used in this investigation was built in this laboratory. It has a voltage increment of 3.75 mv/sec. The polarograms were recorded with a Leeds & Northrup "Speedomax" recorder that had a full scale deflection of 2.5 mv. The dropping mercury electrodes were made from marine barometer tubing obtained from the Corning Glass Works. The electrode used for quantitative determinations had a drop rate of 5.6 seconds with zero applied potential, pH 9.0 at 0°C, and an m value of 1.04 mg/sec.

The electrolysis cell consisted of a jacketed cell through which a cold alcohol-water solution was circulated to maintain the cell temperature at 0°C.

The buffers were prepared according to Clark and Lubs and were 0.1M, unless otherwise noted.

The amines were cp grade chemicals, which were purified further by distillation in the case of aniline, p-anisidine, and p-toluidine.

Solutions of the diazotized amines were prepared from 0.1M amines in a threefold excess of hydrochloric acid. The diazotization was carried out at 0°–5°C and when the reaction was complete, the solutions were diluted to 0.01M with ice cold water.

Polarograms were made upon the deaerated buffer or acid solution at 0°C. Thereupon the required

[1] Manuscript received May 18, 1949. This paper prepared for delivery before the Chicago Meeting, October 12 to 15, 1949.

amount of a solution of diazotized amine was added, nitrogen was passed through to remove dissolved air, and polarograms were run as indicated. At concentrations greater than 10^{-4} molar, pronounced maxima were sometimes observed. Orthner's compound, a commercial surface active agent,[2] was found to be effective in reducing these maxima and was used instead of gelatin. The latter was of only limited value.

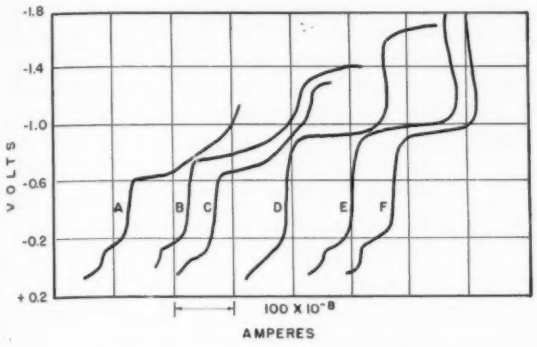

FIG. 1. Polarograms on $2.5 \times 10^{-4}M$ solutions of diazotized aniline at 0°C.

A pH 1.4 C pH 3.9 E pH 7.6
B pH 2.2 D pH 5.9 F pH 10.0

In Fig. 1 there are presented polarograms of diazotized aniline at 0°C at various pH's. These polarograms show that the reduction takes place in two main steps, the first at 0.0–0.3 volts vs. the saturated calomel electrode and the second at a much more negative potential which, unlike the first, does vary with pH. At higher pH's a tendency to maxima formation is to be noted. Polarograms very much like these are obtained with diazotized p-toluidine and p-anisidine. Diazotized sulfanilic acid and 2,5-dichloroaniline present a somewhat different picture, best illustrated by the polarograms on diazotized 2,5-dichloroaniline illustrated in Fig. 2. At low pH's three definite waves are to be noted. In neutral solutions, only two distinct waves are apparent, which correspond very closely to those of diazotized aniline. However, a very pronounced maximum is apparent in the upper wave. In the case of diazotized sulfanilic acid, the maxima in neutral solution are very sharp.

At pH's greater than 9–10 depending upon the diazo (8 in the case of diazotized m-nitroaniline) polarographic reduction of diazotized amines is not observed.

In actual practice satisfactory quantitative results are obtained by measuring only the lower wave which is best done by applying a fixed potential of −0.3 volt vs. S.C.E. Under such conditions linear concentration vs. wave height relationships are obtained as has been shown in the previous publication (1). No surface active agent has been used in such work, and suppression of the maxima has not been used in quantitative work.

In Table I there are summarized some of the results of the polarographic reduction of diazotized aromatic amines. The polarograms are difficult to measure and since the shapes of the waves are irregular the figures for half-wave potential are only of qualitative significance.

TABLE I. *Half-wave potentials of diazotized aromatic amines as a function of pH*

	pH	$E_{\frac{1}{2}}$	
		First wave	Second wave
p-Anisidine diazo	1*N*/HCl	−0.083, −0.184	−0.434
	0.1*N*/HCl	−0.086	−0.524
	4.2	−0.056	−0.575
	7.8	−0.079	−0.919
	9.75	−0.160	−0.930
Aniline	0.1*N*/HCl	−0.18	−0.67
	4.02	+0.029, −0.057	−0.690
	6.02	+0.051, −0.051	−0.920
	8.00	+0.020, −0.154	−0.990
	9.92	−0.202	−0.970
Dichloroaniline	0.1*N*/HCl	−0.106	−0.554, −0.832
	3.92	−0.022	−0.525, −0.875
	5.90	−0.029	−0.802
	7.60	−0.112	−0.820
Sulfanilic	0.1*N*/HCl	−0.326	−0.555, −0.831
	4.02	−0.095, −0.260	−0.626, −0.970
	6.08	−0.112, −0.273	−0.557, −0.885
	7.9	−0.300	−0.606, −0.983
	10.0	−0.233, −0.332	−0.961

[2] General Aniline and Film Corporation Chemical Number 147.

Discussion

The reduction of diazotized aromatic amines at the dropping mercury electrode appears to be a highly irreversible process. This follows from the fact that the shape of the waves is irregular as illustrated in Fig. 1. For this reason, accurate measurements of the half-wave potentials are not possible, and no significance can be attached to the variation of the half-wave potential with pH.

The number of electrons required for the reductions appears to be 4. At a concentration of $2.5 \times 10^{-4}M$ at a pH of 6.79, a current of 1.83 microamperes was obtained. With a $2.78 \times 10^{-4}M$ solution of hydroquinone under the same conditions, a current of 1.0 microamperes was obtained. Since the number of electrons required for the oxidation of hydroquinone is known to be 2.0, the number of electrons required for the diazonium compound becomes 4.06. The total diffusion current is roughly independent of pH so that it is reasonable to suggest that the product of reduction is the hydrazine in all cases.

$$ArN_2^+ + 4e + 3H^+ \rightarrow ArNHNH_2 \qquad (I)$$

This is in agreement with the results of electrolytic reduction of diazonium compounds, as found in the literature (2, 9, 10, 11).

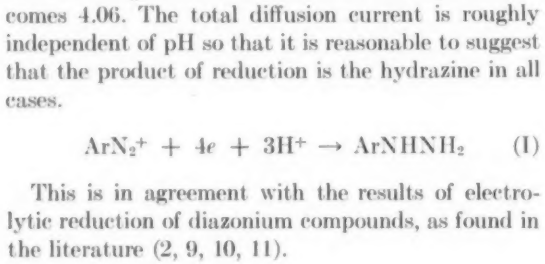

FIG. 2. Polarograms on $2.5 \times 10^{-4}M$ solutions of diazotized dichloroaniline at 0°C.

A pH 1.4 C pH 3.9 E pH 7.6
B pH 2.2 D pH 5.9 F pH 10.0

Although the complete reduction appears to result in the production of a hydrazine, a correct interpretation of the product of the first stage of the reduction cannot be assigned at present. In the first place, this wave is ordinarily about one-half to one-third as large as the second wave but its relative height decreases markedly as the pH increases. Furthermore, its potential is roughly independent of pH while that of the second wave varies markedly with pH. This latter fact might be considered to arise from a reduction according to equation (II).

$$ArN_2^+ + e \rightarrow ArN_2 \qquad (II)$$

in which the reduction product may be stabilized by dimerization or solvation, etc. At higher potentials the reduction goes all the way to the hydrazine. The final stage of the reduction appears to take place in one step in neutral solutions, but in acid solutions still another step may be observed.

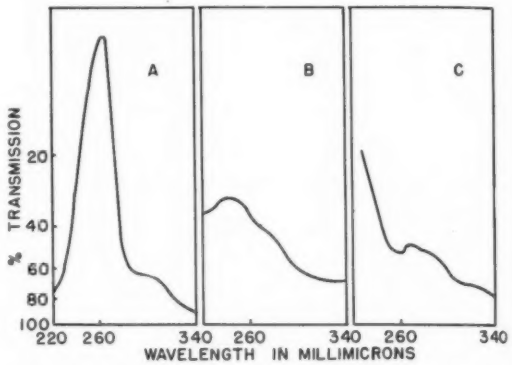

FIG. 3. Ultraviolet absorption spectra at 25°C on diazotized aniline, $1 \times 10^{-4}M$.

A pH 8.0 B pH 10.0 C 0.1*N* NaOH

The polarographic reduction of diazotized aromatic amines is not observed above a pH of 8–10, depending upon the diazo. As might be expected from common coupling practice, the change to a nonreducible form occurs in the negatively substituted diazotized amines at lower pH than with more inactive diazotized amines such as p-anisidine. That this conversion to a nonreducible form is reversible can be easily demonstrated by acidification whereupon a normal polarogram is obtained, provided that the alkalinity has not been too high or too prolonged at a temperature such that ordinary thermal decomposition takes place. The pH at which the polarographic pattern changes corresponds closely with the pH at which the absorption spectrum changes abruptly as shown in Fig. 3. In acid solution and up to pH 8 there is little or no change; above pH 8 the abrupt change is noted. This also corresponds very closely with the point at which the maximum rate of coupling of diazotized aromatic amines with phenols and related compounds is attained. According to Wistar and Bartless (3), who claim that it is the diazonium ion rather than the diazotate that couples, this would indicate that the diazonium ion begins to disappear at this critical pH. Therefore, it may be reasonably concluded that the polarographic waves

arise from the reduction of the diazonium ion to the hydrazine. Diazotates and isodiazotates are apparently relatively if not completely inert at the dropping mercury electrode.

Part II. The Rate of Coupling of Diazonium Salts with Phenols and Related Compounds

Conant and Peterson (4) have studied the rate of coupling of five diazotized aromatic amines with resorcinol and four sulfonated naphthols. The reaction was followed by measuring the change in color of the reaction solutions as the dyes were formed. The method was applicable, therefore, only to systems yielding soluble dyes. A new method has now been developed whereby the rate of coupling of any diazotized amine with any coupler can be measured in the pH range 4 to 9, regardless of the solubility of the dyes formed. The method depends upon the amperometric measurement of the diazo component at the dropping mercury electrode.

In the pH range 0 to 9, solutions of diazotized amines produce well defined diffusion currents at the dropping mercury electrode which are directly proportional to concentration when a voltage of 0.25 to 0.30 volt is applied across the mercury and saturated calomel electrode placed in the solution (1). Azo dyes, with a few exceptions, do not have diffusion currents at this voltage in the pH range 4 to 9. Therefore, a coupling reaction shows a continual decrease of current corresponding to a decrease in diazo concentration as illustrated in Fig. 4. At pH's lower than 4, the diffusion current due to azo dyes interferes to a more or less marked extent. However, it is still possible to follow the reaction under such conditions since the voltage can always be adjusted so that the diffusion currents for the azo and diazo components are not equal for equal concentrations. Under such conditions the current will either increase if the azo break is larger or decrease to a lower value but not to zero, depending upon the applied voltage. The calculation of the reaction velocity constant becomes somewhat more complicated and increasingly inaccurate as the overall change of current approaches zero. Of course, if a highly insoluble dye is produced, no interference even at low pH's would be observed. At a pH above 10 the coupling system can no longer be studied polarographically since the reduction of diazos does not occur.

Apparatus and Preparation of Chemicals

The reaction vessel consisted of a thermostated wide-mouthed bottle having a capacity of 100 ml. This was fitted with a stopper through which was inserted a dropping mercury electrode, a saturated potassium chloride-agar salt bridge leading to a large area saturated calomel electrode, and a nitrogen inlet. The dropping mercury electrode was made from marine barometer tubing of approximately 0.05 mm internal diameter; it had a drop rate of approximately three seconds at zero applied voltage in the various buffers used.

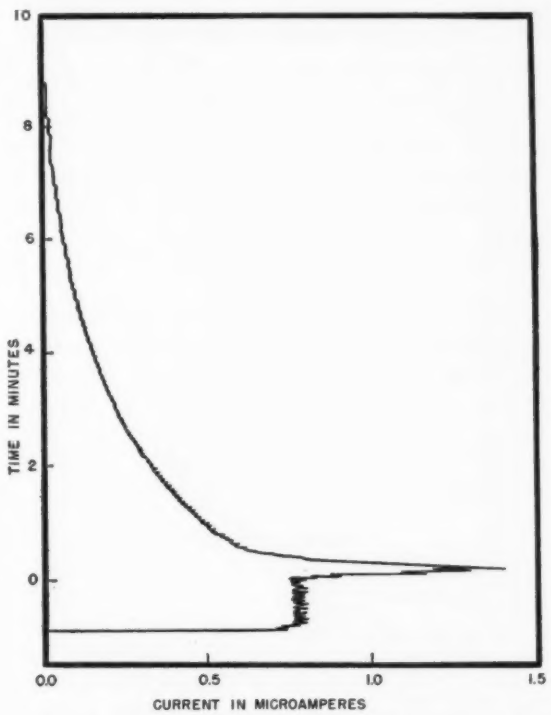

Fig. 4. Amperometric determination of rate of coupling of diazotized p-anisidine, 0.0002*M*, and 3-methyl-1 phenyl-5-pyrazolone, 0.002*M*, in pH 5.4 buffer. Applied voltage 0.3 v vs. saturated calomel electrode; temperature 15°C.

An adjustable voltage was applied across the cell in the usual manner. The current flowing was measured by passing it through a known resistor, usually 1500 ohms, which was connected in turn to a Leeds & Northrup Speedomax Recorder with a range of 0 to 2.5 mv. Oscillations due to the mercury drops were reduced by damping with two electrolytic 1,000 μf condensers connected in series opposed according to Philbrook and Grubb (5).

The couplers were cp grade chemicals which were purified by recrystallization where possible. The amines were cp grade except for o- and m-toluidine and o- and p-anisidine which were purified by careful distillations through a glass helix packed column. The amines were dissolved in 0.4*N* hydrochloric acid to produce a 0.1*M* solution which was diazotized in the usual manner. After the diazotization was completed, the solution was diluted to approximately 0.01*M*. The strength of the resulting solution was

thereupon determined by amperometric titration against pure 3-methyl-1-phenyl-5-pyrazolone, and the solution was diluted again as required (1).

Procedure—The Rate of Reaction of p-Anisidine diazonium chloride with 3-Methyl-1-phenyl-5-pyrazolone

To the reaction cell containing 40 ml of buffer pH 5.4, prepared according to Clark and Lubs, was added 5.0 ml of 0.002*M* p-methoxybenzenediazonium chloride (p-anisidine diazo). The resulting solution was brought to a temperature of 15°C and the dissolved oxygen removed by a current of purified nitrogen. The nitrogen was shut off, and the current recorded with an applied voltage of −0.3 volt. The nitrogen was turned on and 5.0 ml of 0.02*M* 3-methyl-1-phenyl-5-pyrazolone, which was also at 15°C and had been previously swept free of oxygen, was quickly added to the solution.

After about 15 seconds of sweeping to ensure adequate mixing, the nitrogen was turned off and the current recorded as a function of time as illustrated in Fig. 4. The current decreased steadily until it had reached a point of zero current indicating that no diazo was present, and the recorder was reversed to measure any residual negative current.

Calculation of the Results

The coupling rates were usually determined with a tenfold excess of coupler in order to reduce the effect of side reactions such as multiple coupling. Since the diffusion current has been found to be directly proportional to concentration of diazotized amine over the concentration range studied, the chart readings may be taken as a measure of diazo concentration. Therefore, assuming a mole for mole ratio of reaction between diazo and coupler, it becomes a simple matter to calculate the quantity $\frac{b(a\text{-}x)}{a(b\text{-}x)}$. The logarithm of this quantity is then plotted as a function of time, and from the slope of the line the reaction velocity, k, is calculated from the relationship

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \qquad \text{(III)}$$

With the time measured in minutes and the concentration in moles per liter, k has the dimensions of liters moles^{-1} minutes^{-1}. In Fig. 5 is illustrated the plot of log $\frac{b(a\text{-}x)}{a(b\text{-}x)}$ vs. time for the coupling shown in Fig. 4 as well as for the same reaction at pH's 5.2 and 5.6.

In order to obtain a, the initial chart reading, the logarithms of the chart readings have been plotted as a function of time. A straight line is obtained because of the ten to one ratio of reactants and from this the initial chart reading may be deduced. This method automatically compensates for slight changes in the diffusion current due to pH change resulting from addition of coupler, etc. Actually if the reaction is treated as pseudounimolecular, the values of k, deduced from the plot of the log of the chart readings as a function of time, are low by a factor of 5 to 6 per cent which is about the experimental error of duplicate determinations. In Fig. 4 the temporary large increase in current to be noted just after mixing arises from the stirring with nitrogen which increases the diffusion current. When the nitrogen is turned off the current quickly returns to normal values.

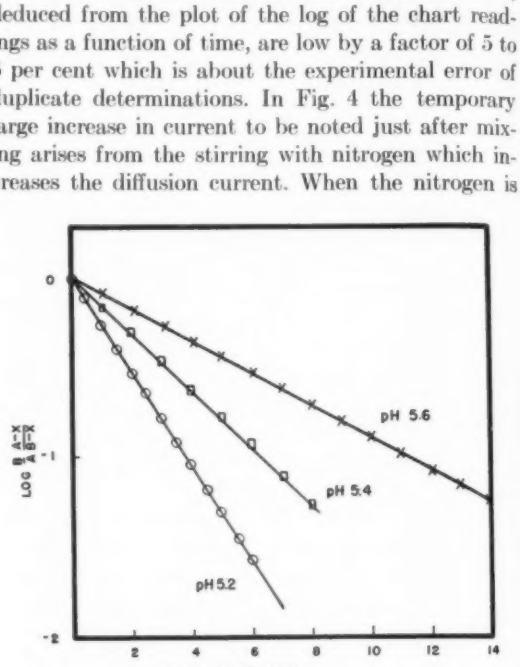

FIG. 5. Kinetics of coupling of diazotized p-anisidine coupled with 3-methyl-1-phenyl-5-pyrazolone at 15°C. ○ pH 5.2, □ pH 5.4, × pH 5.6.

Discussion of the Method

The primary advantage of the new method is that it follows the reaction by measuring the concentration of the diazotized amine. Therefore, it is immaterial whether the product of the reaction is soluble. Since the diazotized amines are all very soluble, it is possible to study the rate of a number of couplings which were difficult to follow by older methods. This procedure may also be applied to the coupling of diazos with colored couplers, such as dyes capable of coupling a second time. Under such circumstances, the colorimetric method may be unsatisfactory because of interference of colors. The method may be used, if precautions are taken, over a considerable range of concentration including ranges where wide departures from Beer's law may make the colorimetric procedure inconvenient.

Fast reactions are comparatively easy to follow. Good data have been obtained on reactions that were 95 per cent complete within two minutes. Slow reactions lasting more than an hour are difficult to follow if a precipitate forms because the dropping mercury

electrode becomes contaminated leading to an irregular drop rate. Reactions may be carried out at virtually any temperature, although at temperatures above 40°C we have noted irregularities which may be associated with convection currents.

A final advantage of the method is that complete data are obtained directly without sampling. If necessary, of course, the automatic recorder may be omitted and a galvanometer used. Under such circumstances data are obtained with very simple and inexpensive apparatus.

Discussion of the Results

Conant and Peterson discovered that the logarithm of the reaction velocity constant k plotted against the pH resulted in a straight line relationship according to equation (IV) where k_0 is a hypothetical reaction velocity, constant at a pH of zero.

$$\log k = \log k_0 + \text{pH} \qquad \text{(IV)}$$

We have found that while a straight line relationship is obtained, at least over the limited range studied here, the slope of this line is not always unity as indicated by equation (IV). Actually Conant and Peterson's data for resorcinol vs. sulfanilic acid do not fit the equation. According to their data, a tenfold increase in k occurs over a pH range of only 0.91 pH units which is in good agreement with our own value of 0.86 pH units. Our results are within 20 per cent of Conant and Peterson's value. This may be considered rather good agreement since Conant and Peterson obtained their data in the presence of a considerably greater salt concentration which, according to them, would increase the reaction velocity constant.

In Fig. 6 are presented some results obtained in this laboratory which illustrate the effect of structure on the coupling reaction. Table II is a summary of results of all the coupling reactions run. The starred values refer to determinations in which the actual pH was not measured but was assumed to be that of the original buffer media. This introduced a possible error of not more than one-tenth of a pH unit. Hence it is necessary to point out that the data are not quite consistent with respect to pH. However, for each pair of reactants, the data are consistent with respect to pH. This inconsistency is chiefly of theoretical importance since modern pH measurements with the glass electrode are dependent on a standard buffer whose pH is limited to about a tenth of a pH. For this reason, i.e., a pH uncertainty of about a tenth of a pH unit, small differences should not be regarded as significant. It will be noticed in column five that many coupling reactions do not follow equation (IV). When log k is plotted against pH, many reactions produce a line with a slope of less than one. Resorcinol particularly does not follow equation (IV).

That the greater effect of pH on couplings with resorcinol as contrasted with 3-methyl-1-phenyl-5-pyrazolone does not arise from multiple coupling can be ruled out by the following consideration. The dye resulting from the coupling of p-toluidine diazo with resorcinol at a pH of 6.8, the highest measured for the pair of reactants, under conditions identical to those under which the coupling rate was measured, was subjected to chromatographic analysis. No evidence for any material corresponding to multiple coupling was found. This was to be expected since

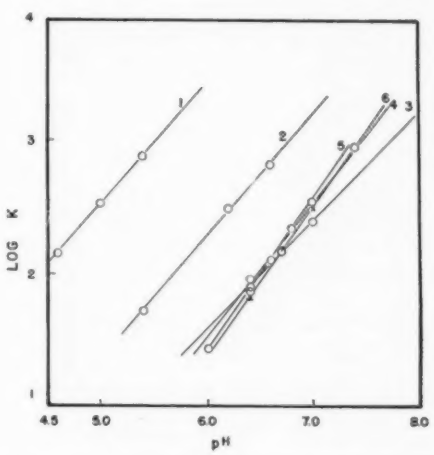

FIG. 6. Logarithm reaction velocity constant vs. pH. 1. Diazotized p-toluidine and 3-methyl-1-phenyl-5-pyrazolone; 2. diazotized p-toluidine and 3-methyl-5-pyrazolone; 3. diazotized p-toluidine and 1-naphthol-5-sulfonamide; 4. diazotized p-toluidine and β-naphthol; 5. diazotized p-toluidine and resorcinol; 6. diazotized p-toluidine and acetoacetanilide.

the very large excess of coupler present should minimize the tendency for multiple coupling. Finally, the agreement of the data presented here with that of Conant and Peterson, who measured the rate of dye formation rather than the rate of disappearance of diazo, confirms the fact that the coupling of resorcinol with diazos is unusually sensitive to changes in pH. It seems likely that the true explanation of the phenomenon lies in the multiple acid dissociation constants K_1 and K_2 of resorcinol. Thus the tendency of the ion ArO_2^- to couple is undoubtedly much greater than that of the ion $Ar(OH)O^-$. According to Wistar and Bartlett (3) the mechanism of coupling is described by equation (V).

$$v = k_1 [ArN_2^+] [ArO^-] \qquad \text{(V)}$$

where v is the rate of reaction and k_1 is a constant. Thereupon at moderate hydrogen ion concentrations

TABLE II. *Reaction velocity constants for coupling reactions*
Temp 15°C

Diazo	Coupler	pH	k Liters moles^{-1} min^{-1}	Slope log k vs. pH
p-Toluidine	3-Methyl-1-phenyl-5-pyrazolone	4.6*	148	
p-Toluidine	3-Methyl-1-phenyl-5-pyrazolone	5.0*	355	1.1
p-Toluidine	3-Methyl-1-phenyl-5-pyrazolone	5.4*	842	
p-Toluidine	3-Methyl-5-pyrazolone	5.4*	53.4	
p-Toluidine	3-Methyl-5-pyrazolone	6.2*	326	1.1
p-Toluidine	3-Methyl-5-pyrazolone	6.6*	703	
p-Toluidine	1-Naphthol-5-sulfonamide	6.4*	80.0	
p-Toluidine	1-Naphthol-5-sulfonamide	6.7*	152	1.3
p-Toluidine	1-Naphthol-5-sulfonamide	7.0*	257	
p-Toluidine	Acetoacetanilide	6.4*	67.7	
p-Toluidine	Acetoacetanilide	6.7*	160	0.89
p-Toluidine	Acetoacetanilide	7.0*	332	
p-Toluidine	Resorcinol	6.0*	26.4	
p-Toluidine	Resorcinol	6.4*	75.5	0.86
p-Toluidine	Resorcinol	6.8*	230	
p-Toluidine	β-Naphthol	6.4*	92.4	
p-Toluidine	β-Naphthol	6.6*	130	1.0
p-Toluidine	β-Naphthol	7.0*	368	
p-Toluidine	β-Naphthol	7.4*	970	
m-Toluidine	1-Phenyl-3-methyl-5-pyrazolone	4.15	88.8	
m-Toluidine	1-Phenyl-3-methyl-5-pyrazolone	4.36	147	0.88
m-Toluidine	1-Phenyl-3-methyl-5-pyrazolone	4.53	245	
m-Toluidine	1-Phenyl-3-methyl-5-pyrazolone	4.76	426	
m-Toluidine	Resorcinol	5.82	67.7	
m-Toluidine	Resorcinol	6.04	113	0.77
m-Toluidine	Resorcinol	6.26	238	
m-Toluidine	Resorcinol	6.48	474	
o-Toluidine	1-Phenyl-3-methyl-5-pyrazolone	4.52	85.8	
o-Toluidine	1-Phenyl-3-methyl-5-pyrazolone	4.70	146	1.0
o-Toluidine	1-Phenyl-3-methyl-5-pyrazolone	4.89	216	
o-Toluidine	1-Phenyl-3-methyl-5-pyrazolone	5.12	343	
p-Anisidine	1-Phenyl-3-methyl-5-pyrazolone	5.2	114	
p-Anisidine	1-Phenyl-3-methyl-5-pyrazolone	5.4	200	0.86
p-Anisidine	1-Phenyl-3-methyl-5-pyrazolone	5.6	333	
p-Anisidine	Resorcinol	6.58	27.3	
p-Anisidine	Resorcinol	6.80	59.5	0.62
p-Anisidine	Resorcinol	7.00	125	
o-Anisidine	1-Phenyl-3-methyl-5-pyrazolone	4.53	82.8	
o-Anisidine	1-Phenyl-3-methyl-5-pyrazolone	5.06	268	0.99
o-Anisidine	1-Phenyl-3-methyl-5-pyrazolone	5.31	500	
o-Anisidine	Resorcinol	5.82	9.4	
o-Anisidine	Resorcinol	6.25	36.7	0.73
o-Anisidine	Resorcinol	6.66	133	
o-Anisidine	Resorcinol	6.88	268	
m-Nitroaniline	Acetoacetanilide	5.0*	991	0.60
m-Nitroaniline	Acetoacetanilide	5.4*	2456	

TABLE II.—*Continued*

Diazo	Coupler	pH	k Liters moles^{-1} min^{-1}	Slope log k vs. pH
Sulfanilic acid	Resorcinol	5.0*	294	
Sulfanilic acid	Resorcinol	5.2*	528	0.82
Sulfanilic acid	Resorcinol	5.4*	914	
Sulfanilic acid	Acetoacetanilide	5.62	239	0.95
Sulfanilic acid	Acetoacetanilide	6.12	1390	

* pH of standard buffer, actual pH not measured.

where the amount of ArO^- is small compared with the concentration of ArOH we have,

$$v = k_1 K_1 [ArN_2^+] \frac{[ArOH]}{[H^+]} = k_1 K_1 \frac{[ArN_2^+](a)}{[H^+]} \quad (VI)$$

where a is the analytical amount of phenol. By taking logarithms of both sides there is obtained

$$\log v = pH + \log v_0 \quad (VII)$$

Restricting the treatment to ArN_2^+ and a being constant, equation (VII) becomes

$$\log k_{measured} = pH + \log k_0 \quad (VIII)$$

This is of course the equation found by Conant and Peterson to describe the behavior of most coupling reactions.

However, for resorcinol the velocity equations would become

$$v = k_1 [ArN_2^+] [Ar(OH)O^-] + k_2 [ArN_2^+] [ArO^-] \quad (IX)$$

where k_2 is a second reaction velocity constant pertaining to the tendency for reaction between ArN_2^+ and ArO_2^-. Again at low pH's where $Ar(OH)O^-$ and ArO^- are small compared with a, there is obtained

$$v = \frac{k_1 K_1 [ArN_2^+](a)}{[H^+]} + \frac{k_2 K_2 [ArN_2^+](a)}{[H^+]^2} \quad (X)$$

Upon taking logarithm on both sides there is obtained

$$\log v = pH + \log \left[1 + \frac{k_2 K_2}{k_1 K_1} e^{2.3pH} \right] + \log v_0 \quad (XI)$$

and

$$\log k_{measured} = pH + \log \left[1 + \frac{k_2 K_2}{k_1 K_1} e^{2.3pH} \right] + \log k_0 \quad (XII)$$

Therefore the slope of line representing the plot of log k measured vs. pH is greater than unity. The actual slope depends upon the factor $\frac{k_2 K_2}{k_1 K_1}$ and pH. The line would not be straight but would be slightly exponential. However, the slope would be reduced below that predicted by equation (XII) at higher pH's because of the previous approximations of $[Ar(OH)O^-]$ and $[ArO_2^-]$. Because of the comparatively short range of pH over which the couplings were measured, the exponential nature of the lines is not noticeable except for the greater slope of the lines as previously noted.

In Table III are listed a number of multiple runs which indicate the precision obtained. However, most of the determinations were not done in duplicate. Instead it was felt that more information could be obtained by varying the pH to see how log k changed. The values reported are probably well within 10 per cent of the true value under the conditions used. Only when the reaction becomes very rapid or very slow would the measurements become less precise. In the case of very fast reactions which are over in about a minute or two, the precision falls off because of time required for mixing and the failure of the recorder to respond fast enough. In the case of reactions which are still measurably incomplete after an hour or more, decomposition of the diazo may occur, which would lead to erroneous results. On the other hand, most of the data were kinetically satisfactory for from 5 to 95 per cent of reaction. Under particularly favorable circumstances, data have been obtained that were kinetically satisfactory for 99 per cent of the reactions.

Part III. Kinetics of Diazotization, Diazo Decomposition, and Diazoamino Hydrolysis

In the preceding section details of the application of the dropping mercury electrode for the measurement of the rate of coupling of diazonium compounds with phenols and related compounds has been described in detail. This section outlines some additional applications of the polarographic reduction of diazotized aromatic amines to the study of diazo chemistry.

Diazotization Rates

Procedure.—Fifty ml of 0.1N HCl containing 2×10^{-4} moles of aniline hydrochloride were placed in an electrolysis cell thermostated at 0°C. A potential of 0.3 volt was applied across the electrodes consisting of a dropping mercury cathode and a saturated calomel half cell connected by a low resistance agar bridge. The cell was swept with pure nitrogen until the dissolved oxygen was completely removed. Two

ml of a previously deoxygenated 0.01*M* solution of sodium nitrite was added to the cell from a calibrated hypodermic syringe. The cell contents were thoroughly mixed for 15 seconds by a rapid stream of pure nitrogen. The nitrogen was then shut off and the recorder turned on. The resulting current is illustrated in Fig. 7. Since the diazotization becomes very slow near the end of the reaction the final concentration of diazotized amine is best obtained by preparing a fresh cell and adding a known amount of diazotized amine instead of nitrite. Thereupon, the concentration of diazotized amine at any time t may be calculated.

TABLE III. *Precision of reaction velocity constants for coupling reactions at 15°C*

Diazo	Coupler	pH	k Liters/mole/min	Mean deviation
m-Toluidine	Resorcinol	6.04	123	
m-Toluidine	Resorcinol	6.04	110	6%
m-Toluidine	Resorcinol	6.04	107	
m-Toluidine	3-Methyl-5-pyrazolone	5.56	146	
m-Toluidine	3-Methyl-5-pyrazolone	5.57	136	
m-Toluidine	3-Methyl-5-pyrazolone	5.57	136	4%
m-Toluidine	3-Methyl-5-pyrazolone	5.57	150	
m-Nitroaniline	Acetoacetanilide	5.0*	894	
m-Nitroaniline	Acetoacetanilide	5.0*	1088	10%

* pH of standard buffer, actual pH not measured.

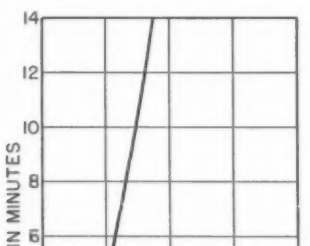

FIG. 7. Diazotization of aniline hydrochloride. 0.1110*N* HCl, temperature 0.5°C.

Calculation and Discussion

As shown by Schmid and Mühr (6), the kinetics of diazotization are somewhat complex. In aqueous sulfuric acid the rate is given by equation (XIII)

$$v = k_1 \frac{[ArNH_3^+][HNO_2]^2}{[H^+]} \qquad (XIII)$$

which may be interpreted to indicate that reaction takes place according to equations (XIV) and (XV) (8).

$$2\ HNO_2 \rightleftarrows N_2O_3 + H_2O \qquad (XIV)$$

$$ArNH_2 + N_2O_3 \rightarrow ArN_2^+ + NO_2^- + H_2O \qquad (XV)$$

By using a tenfold excess of amine, the reaction becomes pseudobimolecular, the integrated form of the reaction-velocity equation becoming,

$$k_1 = \frac{1}{t} \cdot \frac{[H^+]}{[ArNH_3^+]} \cdot \frac{x}{a(a-x)} \qquad (XVI)$$

where x is the amount of diazo at time t and a is the initial concentration of nitrite.

In the presence of halide ion, the diazotization proceeds, in addition to the above mechanism, by reaction with nitrosyl chloride or bromide.

$$HNO_2 + H^+ + Cl^- \rightleftarrows NOCl + H_2O \qquad (XVII)$$

$$NOCl + ArNH_2 \rightarrow ArN_2^+ + Cl^- + H_2O \qquad (XVIII)$$

whence

$$v = [ArNH_3^+]\,[HNO_2]\,[k_1 \frac{[HNO_2]}{[H^+]} + k_2\,[Cl^-]] \qquad (XIX)$$

If the concentration of halide ion is large compared with nitrite ion, the first term in equation (XIX) is small except at the very beginning whence

$$v = k_2[ArNH_3^+]\,[Cl^-]\,[HNO_2] \qquad (XX)$$

and

$$k_2 = \frac{1}{t} \cdot \frac{1}{[Cl^-]} \cdot \frac{1}{(a-b)} \cdot \log \frac{b\,(a-x)}{a\,(b-x)} \qquad (XXI)$$

where a is the initial concentration of amine, b is the initial concentration of nitrite, and x is the amount of diazo formed at time t.

In Fig. 8 is illustrated the results of plotting the data from Fig. 7 to obtain k_2. As might be expected, the resulting data do not quite fit a straight line since at the beginning the first term of equation

(XIX) is not negligible. This is graphically illustrated in Fig. 8 where the results of diazotization of aniline in various concentrations of hydrochloric acid have been depicted. As the chloride ion decreases, the rate not only becomes slower but the data fail to fit a straight line to an increasingly marked extent.

In Table IV are presented the results of diazotization of a number of amines in 0.1*N* HCl which illustrate briefly the effect of structure on the rate of diazotization. As it might be expected, o-anisidine is markedly slower than aniline, and sulfanilic acid and metanilic acid are faster. Both o-anisidine and o-toluidine are distinctly faster than aniline, which is in sharp contrast with the results predicted from the behavior of the p-isomers.

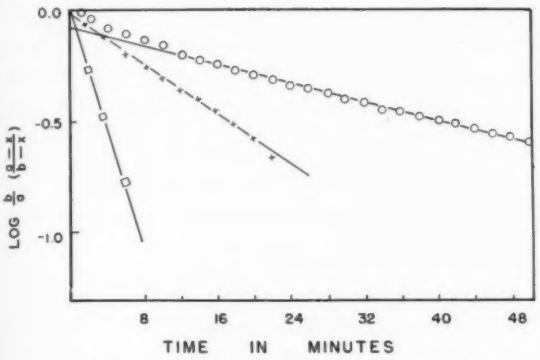

FIG. 8. Kinetics of diazotization of aniline. ○ 0.0278*N* HCl, × 0.1036*N* HCl, □ 0.4731*N* HCl.

It is interesting to note that k_2 is effectively constant over a considerable range of concentration of chloride ion. However, as the halide ion is reduced in concentration, k_1 does tend to increase in importance, as previously discussed. As a result, the calculated value of k_2 does increase slightly as the concentration of chloride ion decreases. These facts are well illustrated in Table V. In order to better illustrate the practical results k_3 has been calculated in this table upon the assumption that the kinetics are described by the equation,

$$v = k_3 [ArNH_3^+] [HNO_2] \qquad (XXII)$$

Diazotization in Acids Other Than HCl

In acids other than halogen acids, the rate of reaction should be independent of the anion and inversely proportional to the hydrogen ion concentration as expressed in equation I.

$$v = k_1 \frac{[ArNH_3^+][HNO_2]^2}{[H^+]} \qquad (XXIII)$$

In Table VI data are presented to show the effect of chloride ions and more particularly bromide ions toward accelerating the diazotization in acids other than hydrochloric acid. It is interesting to note that k_1 in this table is approximately the same for equal concentrations of hydrogen ions whether the reaction was conducted in sulfuric, perchloric, or phosphoric acids.

TABLE IV. *Diazotization of aromatic amines in 0.1N HCl*

Amine	Temp °C	k_2 Liters² mole⁻² min⁻¹
Aniline	0.5	169
	1.0	201
	1.0	167
m-Toluidine	0.5	251
	0.5	265
p-Toluidine	1.0	143
	1.0	146
o-Toluidine	1.0	468
	1.0	472
p-Anisidine	1.0	53.3
	1.0	51.9
o-Anisidine	1.0	443
	1.0	394
Sulfanilic acid	1.0	8,700
	1.5	9,880
Metanilic acid	0.5	2,060
p-Diethylamino aniline	1.0	15,100 (avg of three)

TABLE V. *Effect of HCl concentration on rate of diazotization*

Amine	*N* HCl	Temp °C	k_2 Liter² mole⁻² min⁻¹	k_3 Liter mole⁻¹ min⁻¹
Aniline	.1036	1	191	19.8
	.1036	1	167	17.3
	.4731	1	189	89.3
	.9361	1	Too fast to measure	
	.0278	1	252	7.00
o-Anisidine	.1110	0.5	443	49.6
	.1110	0.5	394	43.7
	.0278	0.5	675	18.7
	.4815	0.5	406	195
Metanilic acid	.1017	0.5	2,060	209.5
	.0185	0.5	2,300	42.7
p-Diethylamino aniline	.0962	1.0	15,100	1,456
	.0130	1.0	17,750	238

Increasing concentrations of H^+ does cause a decrease in the rate of diazotization in agreement with that predicted from equation (I). However, the change was smaller than predicted over a tenfold change in concentration of (H^+) as illustrated in Table III.

Decomposition of Diazotized Aromatic Amines

Just as the dropping mercury electrode can be used to follow the formation of diazonium ions, it can be used to follow the decomposition. The experimental procedure is similar to that for diazotization

except that deaerated diazo is added to a given media instead of nitrite and amine. As the reaction proceeds, the diffusion representing the diazo concentration decreases. That the rate under these conditions is unimolecular is illustrated by the semilog plot of Fig. 9.

TABLE VI. *The rate of diazotization of aniline in various acids*

Temp 1°C

Acid	Normality	pH	*N* Br	k_1 Liter/mole/min	k_2 Liter/mole/min^{-1}
H_2SO_4	.10	1.52	—	274	2.67
	.16	1.39	—	330	2.56
	.10	1.48	.0018	—	30.0
	.018	1.9		200	4.9
$HClO_4$	.10	1.37	—	294	2.25
	.10	1.37	.00018	—	5.76
	.10	1.37	.0018	—	33.4
H_3PO_4	—	1.42	—	366	3.51
	—	1.42	.00018	—	7.52
	—	1.42	.0018	—	34.1
HCl	.0278	1.9	—	—	7.52
	.1036	1.34	—	—	24.7
	.0200	1.97	.0018	—	44.1

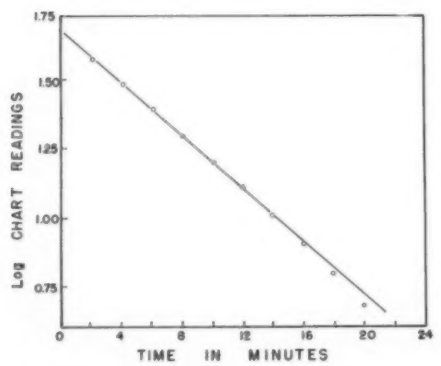

FIG. 9. Kinetics of decomposition of diazotized m-toluidine. pH 1.86, $k = 18.68 \times 10^{-4}$ sec^{-1}.

In acid solutions, pH approximately 1.8, the decompositions are unimolecular as shown by Crossley, Kienle, and Benbrook (7). Furthermore, the results obtained are in satisfactory agreement with the data published by the latter. Thus, for the decomposition of diazotized o-toluidine the rate of decomposition observed was $k = 20.6 \times 10^{-4}$ sec^{-1}. Calculations based on the published values result in a predicted value of 25.6×10^{-4} sec^{-1}.

Whereas previous methods of measuring diazo decomposition have depended upon the formation and measurement of the nitrogen gas evolved, the new method measures the diazo directly. Thus it is possible to measure the rate of decomposition at higher pH's where only a part of the diazotized amine decomposes in such a manner as to form nitrogen gas. Under such conditions, side reactions such as coupling with decomposition products occur, and the kinetics cannot be described by any simple equation. Nevertheless the results can be of practical use for studying the decomposition of diazos because the current records the exact concentration of diazo at any time.

Using similar techniques the decomposition of diazos by light may readily be studied. Under these conditions, however, it is necessary to have either very thin cells or stirring because of the low penetration of the solution by the light.

Diazo-Amino

Diazo-amino compounds are reducible at the dropping mercury electrode, but reduction takes place at much higher voltages than that of the lower wave of diazotized amine. As a result, it is possible to measure the rate of formation and hydrolysis of diazo-amino compounds by following the rate of increase or decrease in diazo concentration using a technique similar to those already described.

As it might be expected, the rate of hydrolysis is accelerated by increasing acidity and increasing temperature as the following results indicate. At a pH of 2.40 and 2°C, the unimolecular reaction velocity constant for hydrolysis of the diazo-amino compound is 1915 min^{-1}. At pH 3.4 and 2°C, $k = 70.3$ min^{-1}, and at pH 3.4 and 22°C, $k = 558$ min^{-1}.

Discussion

The results described in this paper illustrate conclusively that a new technique for studying the chemistry of diazotized aromatic amines is now available. The results obtained have been shown to be in excellent agreement with those obtained by both the gasometric and colorimetric techniques as applied to the various fields of diazo chemistry. It cannot be claimed that the new technique is necessarily the best under any specific conditions, but since it does measure directly the concentration of the diazonium ion it is probably the most versatile. It can be used to follow faster reactions than either the gasometric or colorimetric procedures. On the other hand, very slow reactions are probably better to follow by the conventional methods. As a method for obtaining results with a minimum of effort it is difficult to see how the polarographic method can be surpassed in the study of the kinetics of diazo chemistry. It is to be hoped that the rapidity of the methods outlined can be used to clarify many of the fine points of diazo chemistry.

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1950 issue of the JOURNAL.

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Reactions of β-Pinene[1]

III. Electrolytic Oxidation[2,3]

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ABSTRACT

It is shown that some of the compounds formerly reported to be electrolytic oxidation products of turpentine are not oxidation products but are products of isomerization and hydration. These latter reactions are due to the influence of the emulsifying agents used in the electrolytic process. Other reported products appear to have been present in the original substances used. The effect of electrolytic oxidation on α- and β-pinenes and on cyclohexene under the stated conditions is presented.

INTRODUCTION

The original work on the electrolytic oxidation of turpentine was conducted by Renard (2), who carried out the experiments in an aqueous sulfuric acid-turpentine emulsion using lead dioxide electrodes. He obtained p-cymene, an alcohol whose boiling range was 210°–214°C, a sulfonic acid, $C_{12}H_{24}O_7S$, terpin hydrate, and a resin.

Later Fichter and Schetty (3) oxidized turpentine, of boiling range 155°–159°C, in a similar emulsion and also in an alcoholic sulfuric acid-turpentine emulsion using a lead dioxide anode. They reported the products to be p-cymene, dipentene, cineol, α-terpineol, terpin hydrate, terebic acid, and a resin.

Since the present work was completed, Glasstone and Stanley (4) have reported the effect of temperature, hydrogen-ion concentration, oxygen carriers, rate of stirring, emulsifying agents, and current density on the current efficiency in the oxidation of α-pinene, terpinolene, and dipentene. These investigators used aqueous sulfuric acid as an emulsifying agent. They made no attempt to identify the products formed.

Since none of the prior workers started with highly purified materials, and since it is known that aqueous sulfuric acid is capable of isomerizing and hydrating the pinenes, the present investigation was undertaken to determine which changes were due to oxidation and which were due to the action of the sulfuric acid. During the course of these studies it became apparent that the oxidation of cyclohexene might assist in giving some useful information.

EXPERIMENTAL

The anode compartment was a Coors clay cup (76 x 150 mm) of about 600 ml capacity. It contained the anolyte, a variable speed stirrer, the anode, and a calibrated thermometer that could be read to the nearest 0.1°. A glass hood containing an outlet was placed over the cup. A current of air was sucked through the hood and then through a trap cooled below −20°C. No products were found in this trap.

Experiments were conducted using both platinum and lead dioxide anodes. The platinum gauze anodes consisted of two pieces, 5 x 8 cm each. These were purchased from the J. Bishop Platinum Works. These anodes were bent to fit close to the wall of the clay cup. They rested on the bottom of the cup and were joined together by a piece of platinum wire which served as a common point of contact and, at the same time, held them in place during the rapid stirring of the solution. The anodes were placed opposite each other and at various distances from the walls of the cup, varying from 0 to about 5 mm. The stirrer was in the center and the agar bridge was placed between the stirrer and the anodes.

The lead dioxide anode was made from a lead foil, of unknown source, which was not silver free. The lead dioxide was produced by electrolyzing the lead foil as the anode in a dilute sulfuric acid solution until it was coated with the oxide. It was 20 x 6 cm in area and less than 1 mm in thickness. The foil

[1] For earlier articles in this series, see reference (1).

[2] Manuscript received August 9, 1949. This paper prepared for delivery before the Chicago Meeting, October 12 to 15, 1949.

[3] Extracted from a portion of the thesis of James B. Redd presented in 1943 to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

was slit about every 5 mm and the pieces were bent alternately backward and forward to permit ready circulation of the solution. It was suspended about 1 cm from the bottom of the cup and about 5 mm from the wall. The agar bridge was placed between the anode and the stirrer.

The cathode was a copper sheet having a total surface area of 450 cm^2. This was suspended in a four liter beaker which contained the catholyte, a stirrer, a heater, and a thermoregulator sensitive to about 0.3°. This beaker was placed in a five gallon jar containing water which was cooled by circulating ice water through a Ni-Cu coil.

The voltage applied across the cell was measured within 0.1 volt. The current passing through the cell was measured within approximately 2 per cent.

The electrode potential was measured against a calomel cell using an agar-agar saturated KCl bridge, and a student type potentiometer. It was interesting to note that even with rapid stirring the anode potential was always greater when measured at the top of the anolyte than when measured at the bottom. In all cases the potential, at a given level, between the anolyte and the anode plus that between the anolyte and the cathode was equal to the potential across the cell. The recorded values in all cases were taken at the same level, about 1½ cm from the bottom. From this point down, the measured voltages remained constant.

In order to differentiate between the chemical action of the reagents and the electrolytic oxidation of β-pinene and cyclohexene, duplicate experiments were set up using both β-pinene and cyclohexene. The duplicates were treated in exactly the same manner and for the same length of time except that no current was passed through them.

Tables I and II give the data for all experiments.

Materials

α-pinene was purified by the fractionation of commercial materials,[4] through efficient columns (5). The product had the constants: bp 51.6°C (20 mm), n_D^{25} 1.4631, d_4^{25} 0.8542, which agree with much of the previously published data (6).

β-pinene was obtained by the fractionation of crude material through efficient columns (5) and had the following constants: bp 59.2°C (20 mm), n_D^{25} 1.4768, a_D^{25} −21.4°C. These are in agreement with values (1*b*) obtained heretofore.

The cyclohexene was prepared by allowing commercial cyclohexanol to drip into phosphoric acid at 140°C. The phosphoric acid dehydrated the cyclohexanol and the cyclohexene and water were distilled out as they were formed. Yields were 92–95 per cent based on cyclohexanol. The cyclohexene was separated from the water, washed, and dried over sodium for a day. After fractionation, the cyclohexene had the following constants: bp 83.3°C (760 mm), d_4^{25} 0.806, n_D^{25} 1.4443. These are the recorded values (7).

[4] Furnished through the courtesy of the Southern Pine Division of the Glidden Company, Jacksonville, Florida.

Isolation and Identification of Products

Oxidation of β-Pinene

The liquid from the anode compartment was first tested for aldehydes. None were found.

When an acid anolyte was used, it was neutralized with sodium carbonate and then extracted with ether. The aqueous portion contained the sodium salt of the terebic acid which precipitated upon acidification. It had the following constants: mp 172°–174°C; reported value (8) 174°–175°C; neutral equivalent, found 84, calculated for $C_7H_{10}O_4$, 81. On some occasions evaporation of the mother liquor produced cis-terpin which was identified as described later.

The initial extract was heated to boil off the ether and was then fractionated in a Lecky and Ewell (9) type column. This column was packed with 60 x 60 mesh stainless steel spiral screen. It had an inside diameter of 11 mm. The inner nickel rod had an outside diameter of 2.5 mm. The packing height was 22 inches (56 cm) and had an H.E.T.P. of 0.63 inches (1.6 cm) when tested at atmospheric pressure under total reflux with an n-heptane-cyclohexane mixture.

The distillate contained the hydrocarbons which were refractionated in a Bower and Cook (10) type column. It was 22 inches (56 cm) long and had an inside diameter of 5 mm with an H.E.T.P. of 0.70 in. (1.8 cm) and an operating hold-up of 0.03 ml per plate at optimum throughout rate under atmospheric pressure when tested under conditions as indicated for the Lecky and Ewell column.

α-pinene, β-pinene, and dipentene were obtained at various times.

The α-pinene had the following constants: bp (20 mm) 51°–52°C, n_D^{25} 1.4636. Fuguitt, Stallcup, and Hawkins (6) reported bp (20 mm) 52.2°C, n_D^{25} 1.4631.

The β-pinene had the following constants: bp (20 mm) 59.2°C, n_D^{25} 1.4768, d_4^{25} 0.8665. Fuguitt, Stallcup, and Hawkins reported (6) bp (20 mm) 59.7°C, n_D^{25} 1.4768.

The dipentene had the following constants: bp (20 mm) 72°–73°C, n_D^{25} 1.4705, d_4^{25} 0.8391. Fuguitt and Hawkins (11) reported bp (10 mm) 59°C, n_D^{25} 1.4702, d_4^{25} 0.8387.

The residue from which the hydrocarbons were obtained contained oxygenated compounds. It was treated with twice its volume of ethyl borate to con-

TABLE I. *Data on the electrolytic oxidation of the pinenes*

Expt. no.	Initial weight of pinenes	Electrode composition	Anolyte	Current density amp/cm²	Faradays per mole	Electrode potential	Temp	Products and yields	
	grams					*volts*	*°C*	*grams*	
1	100 α-	platinum	10% H_2SO_4	0.00038	2.1	—	10–18	α-pinene	9.4
								dipentene	4.7
								α-terpineol	8.6
								1:8 cis-terpin	28.4
								polymer	12
2	100 α-	PbO_2 on Pb	10% H_2SO_4	0.00044	4.1	—	20–24	α-pinene	3.1
								1:8 cis-terpin	53.5
								terebic acid	6.2
								polymer	8.4
3	200 β	platinum	Sat. $NaHCO_3$	0.00083	3.9	2.3	23–35	β-pinene	124
								polymer	12
4	200 β-	platinum	Sat. $NaHCO_3$	0.0010	4.6	2.4	23–35	β-pinene	150
								polymer	10
5	190 β-	platinum	Sat. $NaHCO_3$	0.0021	6.0	1.9	25–32	β-pinene	130
								nopinone	20
								polymer	10
6	200 β-	platinum	Sat. $NaHCO_3$	0.0021	6.8	2.7	28–34	β-pinene	104
								polymer	7.5
7	100 β-	platinum	Sat. $NaHCO_3$	0.0019	14.0	2.2	35–38	β-pinene	16.0
								polymer	14.4
8	136 β-	platinum	Sat. $NaHCO_3$	0.0031	14.0	2.8	30–32	β-pinene	115
								polymer	6.0
9	136 β-	platinum	10% H_2SO_4	0.0019	9.2	3.1	25–48	α-pinene	4.1
								β-pinene	19
								α-terpineol	6.0
								terebic acid	13.7
								polymer	15
10	150 β-	platinum	10% H_2SO_4	0.0025	3.3	3.2	20–22	α-pinene	7.0
								β-pinene	92
								dipentene	22
								α-terpineol	2.0
								1:8 cis-terpin	1.6
								polymer	12
11	50 β-	PbO_2 on Pb	Sat. $NaHCO_3$	0.0019	3.0	1.26	25–28	β-pinene	26
								dipentene	3
								pinocarbone	3
								polymer	5.0
12	100 β-	PbO_2 on Pb	Sat. $NaHCO_3$	0.0020	6.8	1.28	25–28	β-pinene	43
								dipentene	8.0
								pinocarvone	9
								polymer	14
13	100 β-	PbO_2 on Pb	10% H_2SO_4	0.0030	11.2	1.90	26–28	dipentene	8.3
								α-terpineol	9.2
								1:8 cis-terpin	28.6
								terebic acid	12.2
								polymer	14.1
14	100 β-	PbO_2 on Pb	10% H_2SO_4	0.0025	6.4	1.80	24–30	β-pinene	9.2
								dipentene	8.0
								α-terpineol	10.9
								1:8 cis-terpin	36.2
								terebic acid	8.1
								polymer	9.0
15	100 β-	None	10% H_2SO_4	0.0	0.0	0.0	25	α-pinene	2.2
								β-pinene	81.2
								dipentene	3.4
								α-terpineol	2.3
								polymer	1.0
16	100 β-	None	Sat. $NaHCO_3$	0.0	0.0	0.0	25–30	β-pinene	92

vert any alcohols to their borate esters and refluxed for two hours on the steam bath. The pressure was decreased to 3-4 mm and the temperature raised to about 150°C in order to remove any neutral oils which might be present.

This neutral oil fraction was treated with about twice its volume of sodium bisulfite according to the method of Schmidt (12). The mixture was extracted twice with ether. The remaining bisulfite solution was treated with sodium carbonate and steam distilled with intermittent additions of sodium carbonate until the runnings were clear. The ether extract of this distillate produced pinocarvone. It had the following constants: bp (8 mm) 88°–89°C, n_D^{25} 1.5019, d_4^{25} 0.987. These are in satisfactory agreement with previously reported values (1*a*). Its semicarbazone melted at 212°–213°C. Stallcup and Hawkins (1*a*) reported 212°–213°C.

TABLE II. *The electrolytic oxidation of cyclohexene* Using a PbO_2 anode, a copper cathode, and anolyte of saturated sodium bicarbonate and a current density of 0.0021 amp/cm²

Expt. no.	Weight of cyclohexene	Faradays per mole	Electrode potential	Temp	Yield of products in grams		
					Cyclohexene	Cyclohexene-1-one-3	Polymer
	grams		*volts*	°C			
1	50	5.2	1.26	25–30	—	4.0	4.0
2	74	5.5	1.30	20–22	4.4	15.5	27.4
3	60	0.0	0.0	25–27	28	0.0	0.0

The ether extract of the sodium bisulfite mixture contained nopinone on one occasion. It was identified by its semicarbazone which melted at 186°–187°C. Baeyer and Villiger (13) reported 188.5°C.

The borate mixture, which remained after the removal of the neutral oils, was hydrolyzed with sodium carbonate and steam distilled. The ether extract of the distillate was distilled through a Bower and Cook (10) column. α-terpineol was obtained at this point. It had the following constants: bp (12 mm) 112°C, n_D^{25} 1.4810, d_4^{25} 0.930. These constants are in line with previously reported values (14). Its phenyl urethane melted at 107°–108°C. Kay and Perkin (14) reported 109.5°C.

The residue from this last steam distillation contained terpin hydrate and the polymer. When the mixture was cooled, the terpin hydrate precipitated and was separated from the polymer which stuck to the sides of the flask. The cis-terpin hydrate when recrystallized from dilute ethanol had a mp of 112°–113°C. A mixed melting point with a known sample gave 112°–113°C. Baeyer (15) reported 116°–117°C for terpin hydrate and 104°–105°C for cis-terpin.

The polymer was not further investigated.

Oxidation of Cyclohexene

The method of separation of the products of the cyclohexene oxidation was the same as described above. No acids were isolated. A careful fractionation of the unoxidized cyclohexene showed no trace of benzene. The physical constants of the low boiling fractions checked those already quoted for cyclohexene. No alcohols could be detected in the borate ester treatment. The neutral oil from the borate ester treatment was almost pure cyclohexene-1-one-3. It had the following constants: bp (20 mm) 64°–65°C, n_4^{25} 1.4808, d_4^{25} 0.965. Marvel and Waltham (16) reported bp (22 mm) 67°–69°C, n_D^{20} 1.4818. Its semicarbazone melted at 164°–166°C, reported value (16) 160°–161°C. A polymer was obtained which was insoluble in the common solvents. It was not further investigated.

Discussion

The total recovery of β-pinene, its isomerization and oxidation products in experiments 7 and 9, is much below what one would expect in view of the recovery in experiments 15 and 16. Apparently, the β-pinene was completely oxidized to CO_2. Tommila (17) states that oxidation at a bright platinum anode often breaks the C—C linkage to give CO_2.

In experiment 5 the platinum electrode in sodium bicarbonate had a potential that was lower than the other oxidations under similar conditions. In this case nopinone was obtained. The result could not be duplicated, and it is possible that a trace catalyst was responsible for the change in the course of the oxidation.

Contrary to the results of Fichter and Schetty (3), no p-cymene was found. It appeared possible that p-cymene might be formed from α- or β-pinene as the result of isomerization and dehydrogenation. This latter step would involve the removal of hydrogen from the ring of an unsaturated cyclic hydrocarbon. To test this point cyclohexene was oxidized electrolytically.

The dehydrogenation of cyclohexene would yield benzene or if the double bond were attacked adipic acid might result. Neither of these was found. Cyclohexene-1-one-3 and a polymer were formed. It does not appear, therefore, that p-cymene is a product of the electrolytic oxidation of α- or β-pinene.

Both p-cymene and cineol have been reported as constituents of some turpentine by Chadwick and Palkin (18). It is suggested, therefore, that the p-cymene and the cineol reported by Fichter and Schetty (3) as products of the electrolytic oxidation of turpentine were already present in their starting material.

Separate experiments verified the formation of α-

terpineol and dipentene as isomerization and hydration products in the presence of sulfuric acid. While 1:8 terpin appeared in the experiments when current was passed through the mixture containing sulfuric acid, the well-known relations (19) between dipentene, α-terpineol, terpin, and terpin hydrate indicate that the terpin was not the result of direct electrolytic oxidation. Local heating effects at the anode would account for its formation. This same heating effect might explain the presence of dipentene in experiment 11 while no dipentene was found in experiment 16.

It is concluded that under the conditions of the experiments herein reported the only electrolytic oxidation products of α- and β-pinene in aqueous H_2SO_4 emulsions are terebic acid and a resinous material. In aqueous $NaHCO_3$ a resinous material and pinocarvone or nopinone are electrolytic oxidation products of β-pinene.

Summary

1. Terebic acid and a resin are the main electrolytic oxidation products of α- and β-pinene under conditions used by Fichter and Schetty.

2. It was shown why the α-terpineol, dipentene, and 1:8 cis-terpin hydrate, identified by Fichter and Schetty as oxidation products, should be considered isomerization and hydration products.

3. Cineol and p-cymene could not be isolated in the present experiments and it is concluded that these were probably present in the starting material of Fichter and Schetty.

4. The higher the oxidation potential using platinum anodes in 10 per cent sulfuric acid and in saturated bicarbonate solution, the more completely β-pinene is oxidized.

5. At the lower oxidation potentials used with lead dioxide on lead electrodes, in saturated sodium bicarbonate solution, β-pinene was oxidized to pinocarvone and cyclohexene was oxidized to cyclohexene-1-one-3.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1950 issue of the Journal.

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The Electrolytic Reduction of Salicylic and Acetylsalicylic Acids to the Corresponding Aldehydes[1]

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ABSTRACT

The electrolytic method for reducing salicyclic acid to salicylaldehyde has been reinvestigated, and the apparatus and procedure recommended by Tesh and Lowy has been used as a standard with which to compare new evidence. Sodium bisulfite was used for fixation of the aldehyde and a 15°–18°C reaction temperature was maintained.

The results of Tesh and Lowy, which have been questioned by some investigators, were substantiated. The necessity for using boric acid in the catholyte was shown and the possibility of using a different type of apparatus was demonstrated.

The method has been applied to acetylsalicylic acid to produce acetylsalicylaldehyde in 25 to 30 per cent yield.

INTRODUCTION

Salicylaldehyde, or o-hydroxybenzaldehyde, is manufactured on a rather substantial scale as an intermediate in the synthesis of the important perfume and flavoring material, coumarin. Two processes are currently employed in the industry to produce this aldehyde. The oldest method consists of treating phenol with chloroform and sodium hydroxide. A mixture of ortho- and para-isomers is obtained in which the ortho predominates and can be separated from the para-isomer by steam distillation. Also encountered industrially is the process starting with ortho-cresol, which is somewhat analogous to the process by which benzaldehyde is made from toluene. Coumarin is subsequently prepared from salicylaldehyde by the Perkin reaction.

Since salicylic acid is a relatively cheap material and is readily obtainable, a process for reducing this material directly to salicylaldehyde would obviously be quite desirable. The reduction of an acid to the corresponding aldehyde is, however, attended by many difficulties, and the only process of this kind of any importance involves the reduction (in water solution) of the sodium salt of the particular acid with sodium amalgam, which may be produced continuously electrolytically using a mercury cathode. This method, however, has the advantage over the Reimer-Tiemann method in giving the single desired isomer, and the yield is also improved.

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The literature cites several examples pertaining to the preparation of benzaldehyde and salicylaldehyde by this method (7, 10, 12, 14, 15) as well as by the purely chemical process (1, 16) wherein metallic sodium is introduced directly into mercury to produce the amalgam.

The earliest reference to the electrolytic reduction of salicylic acid to salicylaldehyde appears to be a process patented by Hugo Weil in 1906 (15). Two years later Carl Mettler (10) described a process almost identical to Weil's for electrolytically reducing the sodium salts of benzoic and salicylic acids to the corresponding aldehydes in 30 to 50 per cent yield. Another contribution by Weil in 1908 described a process (16) using 2 per cent sodium amalgam; a yield of 60 per cent was claimed. Davies and Hodgson (1) report a 64 per cent yield of salicylaldehyde.

The most complete and thorough research carried out to date on the electrolytic reduction of salicylic acid to salicylaldehyde has been that of Tesh and Lowy (14), who reported that by following Mettler's specifications they were able to obtain a yield of only 20 per cent. To increase this yield and to work out the details of the process which had been omitted by both Weil and Mettler, Tesh and Lowy undertook an extensive study of the numerous variables involved. Their most significant contribution was to recommend the use of sodium bisulfite to combine with the newly-formed aldehyde to protect it from further reduction to the alcohol. Their best yield was reported as 55 per cent. (Because they used a molecular weight of 140, rather than 138.12, this

yield should be reduced to 54.2 per cent and other values should be reduced by the same factor.)

Rutovskii and Korolev (12) reported in 1928, on testing the electrolytic reduction of salicylic acid according to Weil and also Tesh and Lowy, that the methods gave yields only up to 34 per cent of the theory and then only if all experimental conditions were strictly observed. They also pointed out that stirring is of great importance. Kawada and Yosida (7) have reported on a similar procedure wherein the only significant difference was the addition of borax to the catholyte, but a yield of 80 per cent was claimed. These several papers reporting such a wide variation in yield of this important chemical intermediate call for a reinvestigation to determine if an 80 per cent yield can be obtained. It was further desired to carry out this reduction on acetylsalicylic acid (aspirin), since the corresponding aldehyde might be expected to yield coumarin directly through dehydration.

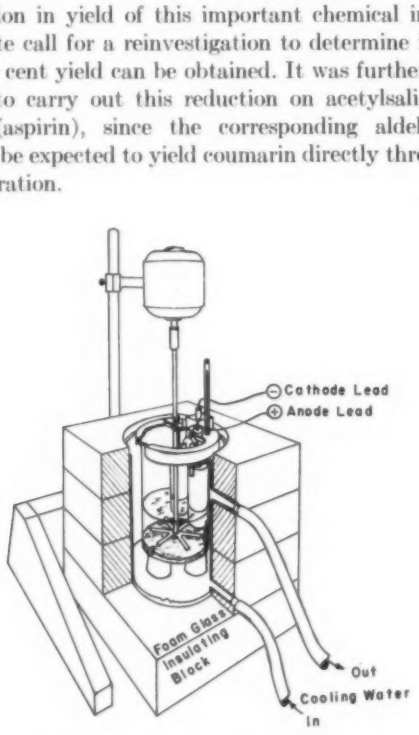

FIG. 1. Basic or standard reduction cell

APPARATUS

Basic or Standard Reduction Cell

The major portion of the experimental work of this research was carried out in apparatus which differed only in minor details from that described by Tesh and Lowy. The electrolytic cell consisted of a 600 ml beaker in the bottom of which was placed 25 ml of mercury to serve as the cathode. Lead strips were employed as anodes, and the anolyte was contained in two porous cups [1 in. x 2.75 in. (2.5 x 7 cm) alundum extraction thimbles], which served also as diaphragms and were suspended so that the bottom of each was two centimeters above the surface of the mercury. Additional details are shown in Fig. 1.

Modifications in the Basic Apparatus

The basic apparatus just described was modified to a greater or lesser extent in several experiments to explore a few of the possibilities for design of full scale equipment. Two distinctly different possibilities exist. First, a cell consisting of all the conventional elements might be retained in which case the prime consideration would be the reduction in the quantity of mercury required. Second, equipment might be designed in which the amalgam would be generated in a separate cell similar to the German vertical cell (2) or the Mathieson Chemical Corporation cell (3), and the reduction would subsequently be carried out in a separate reactor or decomposing tower.

In the first case, experiments were conducted by substituting a thoroughly cleaned and amalgamated sheet of lead or iron for the mercury layer. In the case of the sheet iron, a mercury film or amalgam was obtained only after, but immediately upon, passage of current. Any excess of mercury was then decanted from the metal.

In the second case, an electrolytic cell similar to and of the same size as the basic cell was set up to produce sodium amalgam for use in a fixed surface (beaker) type reactor with stirrer or in a 16 mm jacketed glass tubing decomposing tower or reactor packed with 2 ft (61 cm) of 3 mm glass beads through which the amalgam and reaction mixture were passed counter-currently. A bottom drawoff tube with an adjustable seal leg maintained a constant mercury level in the cell by forwarding amalgam to the reactor as the denuded mercury was manually returned to the cell at a rate of about 2 ml per minute.

One further modification of the Tesh-Lowy apparatus was made for the express purpose of raising the yield, and in this instance, the electrical circuit alone was changed. It was thought that the yield and current efficiency might be improved if a better balance could be struck between the rate of reaction and the rate of electrolysis. To accomplish this end, a simple commutator was introduced into the circuit to furnish an interrupted or intermittent direct current.

EXPERIMENTAL PROCEDURE

The procedure followed in a majority of the experiments of the present research involved only minor changes from the Tesh-Lowy method. To 155 ml of distilled water there were added, in the order listed, with stirring until each constituent dissolved, 4.0 grams (0.1 mole) sodium hydroxide, 14.0 grams (0.103 mole) salicylic acid, 15.0 grams sodium sulfate, and 15.0 grams boric acid. Unless otherwise indicated in Table I, a total of 20 grams sodium bisulfite were also added to the above catholyte mixture at 10 minute intervals during the electrolysis.

The anolyte consisted of 25 ml of 10 per cent sodium sulfate solution.

When aspirin was investigated, 18.0 grams (0.1 mole) were used and the entire catholyte was filtered before introduction into the cell.

after the current was shut off in order to utilize any residual amalgam.

At the conclusion of the electrolysis, the porous cups were removed, rinsed, and any precipitate collected thereon scraped off and returned to the catho-

TABLE Ia. *Effect of stirring upon yields of standard (Tesh-Lowy) method*
3 amp for 1 hr 55 min

Expt. No.	Stirrer	Speed	Volts average	Material balance, grams			Yield % of theo.	Current efficiency	Conversion
				Sal. ald.	Sal. acid	Tar			
								%	%
3	1	mod. high	15.0	4.0	2.0	2.0	37.7	30.5	32.3
8*	1	mod. high	13.5	4.6	1.5	3.0	41.7	35.1	37.2
9	1	mod. high	13.5	4.5	1.5	3.0	40.8	34.4	36.4
10	2	mod. high	15.5	3.7	0	3.0	29.9	28.2	29.9
11	3	60 rpm	12.5	4.6	5.0	0.5	57.9	35.1	37.2
13*	3	60 rpm	14.0	4.6	2.8	0.5	46.5	35.1	37.2
14†	3	60 rpm	12.5	4.7	1.5	3.5	42.6	35.9	38.0
16†	3	250 rpm	15.0	6.1	0	0.7	49.3	46.5	49.3
17†	3	400 rpm	14.0	1.8	6.9	2.1	28.7	13.7	14.5

* Fresh triple distilled Hg used.
† Quantity of Hg reduced to 25 cm³ and 3/16 in. (4.7 mm) depth.
Stirrer No. 1—Bent glass rod located off center of cell.
Stirrer No. 2—Propeller type 1 in. (2.5 cm) diameter located off center of cell.
Stirrer No. 3—Glass rod spider with 6 spokes 2.6 in. (6.5 cm) diameter located at center of cell beneath anode cups.

TABLE Ib. *Comparison of steam distillation and ether extraction procedures for recovery of salicylaldehyde from reaction mixture*

18	Steam dist'n.	12.5	5.0	1.3	2.5	44.6	38.2	40.4
19	Ether extraction	12.5	4.4	2.2	1.4	42.2	33.6	35.6

TABLE Ic. *Effect of current density upon yield*

Expt. No.	Current density	Time	Volts average	Material balance, grams			Yield % of theo.	Current efficiency	Conversion
				Sal. ald.	Sal. acid	Tar			
								%	%
21	4 amp/dm²	2 hr 52 min	11	4.5	4.0	2.0	51.0	34.4	36.4
23	7 amp/dm²	1 hr 39 min	13.5	5.8	1.0	1.5	50.5	44.3	46.8
25	8 amp/dm²	1 hr 26 min	15.0	6.0	1.0	2.0	52.3	45.8	48.5

TABLE Id. *Effect of intermittent electrolysis—interrupted current*

27	54 cycles/min	13.0	2.3	6.5	2.0	34.7	35.1	18.6
28	108 cycles/min	14.5	2.8	4.5	1.9	33.4	42.7	22.6
29	216 cycles/min	13.0	2.6	5.0	2.0	32.7	39.7	21.0

TABLE Ie. *Effect of time upon yield*

	Time	Stirring rate						
32	1 hr	60 rpm	11.5	2.5	2.0	1.5	23.6	36.6	20.2
33	55 min	250 rpm	14.0	2.9	4.5	1.0	34.6	46.2	23.4
34	3 hr 50 min	250 rpm	12.0	6.3	0	2.5	51.0	24.0	51.0

After assembling the cell and cooling the contents to 15°–18°C, electrolysis was conducted at 3 amperes for 115 minutes as specified by Tesh and Lowy. Stirring of the solution was continued for 30 minutes

lyte solution which was separated from the mercury by means of a separatory funnel. The mercury was washed with two 50 ml portions of distilled water and the washings added to the catholyte mixture,

to which was also added 20 ml of concentrated sulfuric acid diluted to 100 ml with distilled water.

tained was made and this value was converted to a weight basis by applying a density factor of 1.15 grams/ml. The residue from the steam distillation

TABLE If. *Influence of $NaHSO_3$ addition rates and concentration in catholyte upon yield*

Expt. No.	Conditions	Volts average	Material balance, grams			Yield % of theo.	Current efficiency	Conversion
			Sal. ald.	Sal. acid	Tar			
							%	%
35	20 g $NaHSO_3$ added at beginning of electrolysis*	11.0	3.1	5.2	2.0	39.9	23.7	25.0
36	20 g $NaHSO_3$ and 10 g H_3BO_3 at start; 5 g H_3BO_3 after ½ hr*	12.0	3.5	3.9	2.2	39.2	26.7	28.2
37	20 g $NaHSO_3$ and 7.5 g H_3BO_3 at start; 7.5 g H_3BO_3 after 45 min*	12.5	3.2	5.0	2.5	40.2	24.4	25.8
38	5 g $NaHSO_3$ at start; 8 g $NaHSO_3$ added at uniform rate during electrolysis†	12.0	5.2	3.0	1.5	53.5	39.7	42.0

* No. 1 stirrer.
† No. 3 stirrer at 250 rpm.

TABLE Ig. *Dependency of yield upon relative concentrations of boric acid and sodium bisulfite*

Expt. No.	Boric acid	$NaHSO_3$	Volts average	Material balance, grams			Yield % of theo.	Current efficiency	Conversion
				Sal. ald.	Sal. acid	Tar			
								%	%
42	none	40 g	9.5	0	—	0	—	0	0
43	none	20	10.0	0	—	0	—	0	0
45	37.2 g	(Na_2SO_3, equiv. amt.)	12.0	5.5	—	1.5	44.5	42.0	44.5
46	6.2	26	12.0	2.8	5.3	1.8	36.5	21.4	22.6
47	9.3	23.4	12.0	4.3	3.0	2.5	44.3	32.8	34.8
48	12.4	20.8	12.0	5.4	1.0	1.1	47.1	41.2	43.6
49	15.5	18.2	11.0	6.2	0	1.8	50.1	47.4	50.1
50	18.6	15.6	12.0	6.0	0	1.5	48.5	45.8	48.5
51	21.7	13	12.5	5.9	0	2.0	47.7	45.0	47.7
52	24.8	10.4	13.0	5.5	0	2.0	44.5	42.0	44.5

TABLE Ij. *Electrolytic reduction of acetylsalicylic acid or aspirin*

Expt. No.	Conditions	Volts average	Material balance, grams			Yield % of theo.	Current efficiency	Conversion
			Ald.	Acid	Tar			
							%	%
78	1 hr electrolysis; steam dist'n.	11.5	2.2*	8.6†	0.3	47.8	32.2	18.0
79	no boric acid	11.5	0		0		0	0
80	10 g borax to catholyte	11.5	3.1*	0	1.3	25.4	23.6	25.4
81	18.6 g H_3BO_3 15.6 g $NaHSO_3$	11.0	3.0*	4.3†	1.2	35.7	22.9	24.5
82	10.4 g $NaHSO_3$	10.5	3.8*	0	1.5	31.1	29.0	31.1
83	10.4 g $NaHSO_3$; catholyte sat'd. with SO_2 to ppt. acetylsalicylic acid; filtrate acidified and extracted with ether	12.5	2.9	5.0	—	24.5	16.5	17.6

* Salicylaldehyde.
† Salicylic acid.

The acidified mixture was then steam distilled until no further oil came over. Oil and distillate were separated and the distillate subjected to repeated steam distillations until no further oil could be obtained. A volumetric measurement of all the oil obwas allowed to cool and was later filtered to recover any salicylic acid and to determine the quantity of tar.

Although the above procedure applies specifically to the standard experiment, which is designated

throughout this work as the standard procedure or Tesh-Lowy method, it applies in a general way to all the experiments conducted. Any deviations from this procedure are indicated in Table I.

Discussion

Table I summarizes the results and experimental conditions of the present investigation.

It will be noted that columns are included for percentage yield, current efficiency, and percentage conversion. These quantities are closely related and in many instances may be numerically identical. The percentage conversion is defined here to be the percentage of starting material converted to salicylaldehyde (or acetylsalicylaldehyde), whereas yield is calculated on the basis of aldehyde obtained as compared to the net quantity of acid used. The current efficiency would normally be (for 0.1 mole quantities) numerically identical to the percentage conversion except for the fact that, in accordance with the specifications of Tesh and Lowy, a slightly longer than theoretical time interval for electrolysis was used. Also, in calculating yield, Tesh and Lowy did not consider the quantity of acid recovered, so in general the yield figures of Tesh and Lowy correspond to percentage conversion as presented in Table I.

It was attempted in this work to account for all the material used, but in the majority of experiments it was possible to account for only about 75 per cent of the salicylic acid used. Also, the low current efficiencies cannot be readily explained. Hydrogen evolution was plainly evident in many instances, but in other cases, there appeared to be practically no evolution of hydrogen so that the low efficiency cannot be accounted for in this manner. The possibility that other unidentified materials may have been produced seems to be a plausible explanation for both low current efficiency and poor material balance.

Influence of Various Factors in the Electrolytic Reduction of Salicylic Acid to Salicylaldehyde

Although the highest yield of salicylaldehyde as reported by Tesh and Lowy was approached fairly closely, it was never quite attained. Reference to Table I will show that many results were obtained in the 35 per cent yield range; and hence, it is readily seen how certain investigators (12) concluded that 34 per cent yield was the maximum obtainable. In fact, the 55 per cent yield reported by Tesh and Lowy was included but twice and both entries in their table of results appear to be for the same experiment.

When the specifications of Tesh and Lowy are adhered to closely, the conclusion is drawn that proper stirring is of controlling importance. There appears to be for any particular stirrer an optimum speed for best mixing the catholyte and moving fresh solution past the mercury surface without disturbing this surface. The mercury can become "poisoned" with low overvoltage elements thereby giving rise to low yield, but this source of trouble may be easily eliminated, and studies (Table I*a*) in which such influences have been eliminated point to the importance of proper stirring and proper cell design.

The method employed to recover the aldehyde from the electrolyzed solution might be expected to have considerable bearing on the yield especially with respect to tar formation during steam distillation. As shown in Table I*b* steam distillation suffers no disadvantage in this regard as compared to extraction procedures. Tesh and Lowy have recommended extracting the distillate with ether to recover all the available aldehyde. It was found preferable, however, to steam distill repeatedly the separated distillate both from a standpoint of convenience of operation and of total aldehyde recovery.

A study of current density (I*c*) corroborated the results of Tesh and Lowy and indicated an independence of yield and current efficiency with respect to current density over a rather wide range of operation. A further attempt (I*d*) to bring the rate of electrolysis into better balance with the reduction rate of the salicylic acid by the introduction of a commutator in the electrical circuit to provide an intermittent direct current gave results no different from those obtained by the usual procedure.

In order to ascertain the effect of time upon yield, several experiments (I*e*) were conducted for one half the normal period of electrolysis and, in one instance, for twice the normal time. The amount of tar formed was not significantly different in any case in contradiction to what might be expected. A higher yield would be expected during the first hour of electrolysis but actually lower yields were obtained. Of more importance, but unexplained significance, is the fact that only the usual conversion of acid to aldehyde was obtained in the double length experiment along with about the usual amount of tar. Variations in the addition of sodium bisulfite (I*f*) both as to rate of addition and concentration held in the catholyte also appeared to be without appreciable effect on the amount of tar formation.

The most significant findings of the present research relate to the dependence of yield upon the use and relative concentration of boric acid. Reference is made in the Weil patent (15) to the surprising observation that sodium salicylate is reduced in aqueous solution with greater ease in the presence of free boric acid. According to Mettler (9) the presence of free boric acid stops the reduction of the acid at the aldehyde in the electrolytic method when a mercury cathode is used and also in the purely

chemical method when sodium amalgam is used. Aromatic aldehydes in alkaline solution are also reported (4) to yield hydroxybenzoin derivatives. It would be concluded from this information that the chief purpose of the boric acid would be to maintain faint acidity and thus control the course or extent of reduction.

This conclusion does not appear, however, to be reasonable since the addition of excess sodium bisulfite both maintains acidity of the catholyte and stops the reduction at the aldehyde. It may be possible that a critical pH range may exist which is maintained by the buffer action of boric acid and the associated system but this does not seem too probable. It seems much more likely that the explanation

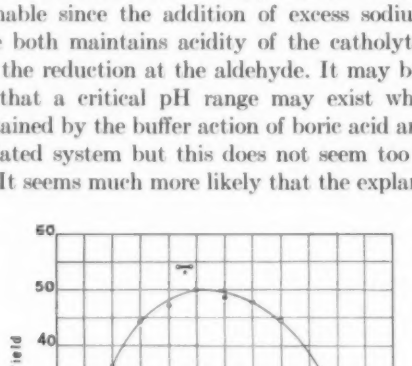

FIG. 2. Relationship of yield to relative concentrations of boric acid and sodium bisulfite. *Tesh-Lowy maximum yield—0.121 equivalents boric acid, 0.192 equivalents sodium bisulfite.

lies in the formation of a complex salt formed between boric acid and sodium salicylate.

Hermans (5), Meulenhoff (11), and Schafer (13) have all reported the preparation of borosalicylates and Loomis (8) was granted a patent for a process of producing salicylaldehyde by treating acid sodium borodisalicylate with sodium amalgam in the presence of sodium sulfite or bisulfite.

Table I*g* shows conclusively the need for boric acid. It has also been demonstrated (I*g*-45) that sodium sulfite is as effective as bisulfite in protecting the aldehyde from further reduction. This observation enabled a study of the boric acid-bisulfite relationship when the total acidity thus introduced was held equivalent to the total possible alkalinity. Fig. 2, based upon experiments I*g*-46 to I*g*-52, shows that an optimum relationship resulting in maximum yield exists at approximately the specifications used by Tesh and Lowy and originally set forth by Weil and Mettler.

Modifications in Apparatus Directed Toward the Design of Full Scale Equipment

Although an improvement in yield was not effected by any of the experimental conditions investigated, some thought was given to the design of commercial scale equipment. As specified by Tesh and Lowy, a considerable inventory of mercury would be indicated. It has been found that this inventory can be reduced to an absolute minimum. As a means of doing this, the mercury in the Tesh-Lowy apparatus was replaced in one instance by an amalgamated lead sheet and in a second instance by an amalgamated piece of sheet iron. Comparatively the amalgamated sheet iron performed much more satisfactorily than did the amalgamated lead sheet indicating the need for a continuous mercury film. The German vertical caustic cell (2), which employs the film principle, illustrates a type of construction which, with the introduction of diaphragms and certain other modifications, might possibly be advantageously adapted to the electrolytic reduction process.

A more practical approach to commercial operation would probably be to generate the sodium amalgam in a separate cell such as the German cell or the Mathieson Alkali Corporation cell (3) and to carry out the reduction step in a separate reactor. The initial attempts along this line were unsuccessful. Graphite anodes had been employed in the electrolytic cell and it is believed that the slight disintegration of these anodes furnished sufficient material to keep the amalgam concentration below a critical value. On repeating these experiments and substituting lead anodes for graphite, the results were much more satisfactory. The tower type reactor appeared to be superior to the fixed surface type in yield and is definitely so with respect to simplicity of construction. Many considerations have yet to be investigated in this regard, but it has been demonstrated at least that the method is workable and that it warrants additional effort.

The Electrolytic Reduction of Acetylsalicylic Acid

Group *j* of Table I summarizes the experiments performed in studying the reduction of acetylsalicyclic acid to acetylsalicylaldehyde. The advantage of starting with aspirin would be, of course, the elimination of the step introducing the acetyl group into salicylaldehyde to obtain coumarin.

In general, all the observations made in the reduction of salicylaldehyde apply to the reduction of acetylsalicylaldehyde. The solubility of boric acid in the acetylsalicylic acid catholyte is not as great as for salicylic acid, but its presence is nevertheless essential to carry out any reduction.

The ease with which acetylsalicylic acid and acetylsalicylaldehyde undergo hydrolysis complicates

the study of these materials. For this reason, it was more convenient to hydrolyze the acetylsalicylaldehyde to salicylaldehyde during the steam distillation and thus to determine yields. However, to establish the synthesis of acetylsalicylaldehyde as such, the reaction mixtures were in two instances extracted with ether after first precipitating the residual acetylsalicylic acid with sulfur dioxide and then acidifying to break down any sulfite-aldehyde complex. In both cases, a material was obtained which melted between 35° and 39°C as compared to 38°–39°C as reported in Heilbron (6) for acetylsalicylaldehyde. While this by no means can be considered as identification, it would appear reasonable that acetylsalicylaldehyde was actually obtained. Regardless of positive identification the yield of acetylsalicylaldehyde is too low to be of any commercial interest, but academically, at least, the method apparently presents a new synthesis for this material.

Conclusion

The present investigation has substantiated the work of Tesh and Lowy on the reduction of salicylic acid to salicylaldehyde thereby disproving the limitation of the electrolytic method to the lower yields reported by other workers. The attainment of appreciably higher yields, likewise, has been shown to be improbable.

The presence of boric acid is a prime requisite in the reduction of both salicylic and acetylsalicylic acids and the proper stirring of the catholyte is of very considerable importance.

Any discussion in this paper will appear in a Discussion Section, to be published in the December 1950 issue of the Journal.

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